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Exposure and Risk Assessment for Dichlorobenzenes (1,2-Dichlorobenzene 1,3-Dichlorobenzene, 1,4-Dichlorobenzene) (Revised)

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16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in March of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of dichlorobenzenes in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to dichlorobenzenes for various subpopulations.

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AN EXPOSURE AND RISK ASSESSMENT FOR DICHLOROBENZENES

1,2-Dichlorobenzene

1,3-Dichlorobenzene

1,4-Dichlorobenzene

by

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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

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Office of Water Regulations and Standards

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The materials balance for the dichlorobenzenes (Chapter 3.0) was produced by Acurex Corp., under contract 68-01-6017 to the Monitoring and Data Support Division (MDSD), Office of Water Regulations and Standards (OWRS), U.S. Environmental Protection Agency. Kenneth Moss was the task manager for Acurex, Inc. Patricia Leslie was responsible for report production.

Gregory Kew, MDSD, was the project manager at EPA.

1.0 TECHNICAL SUMMARY

1.1 INTRODUCTION

The Monitoring and Data Support Division, Office of Water Regulations and Standards, U.S. Environmental Protection Agency is conducting an ongoing program to identify the sources of and evaluate the exposure to the 129 priority pollutants. This report assesses the exposure to and the probable risk associated with exposure to 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene. The organization of this summary is somewhat different from that of the report, focusing on the risk considerations first since this section presents the major conclusions of the study.

1.2 RISKS TO HUMANS AND AQUATIC ORGANISMS

Dose levels at which acute effects have been observed in humans or mammals are generally more than three orders of magnitude greater than the typical levels of human exposure through inhalation and ingestion. The potential chronic effects of dichlorobenzenes have yet to be determined. The dichlorobenzenes are considered by the Carcinogen Assessment Group of the U.S. EPA to be of potential concern with respect to carcinogenicity; however, the available data on carcinogenic, mutagenic or teratogenic effects are not sufficient at this time to permit a quantification of these risks to humans. Existing health effects data from subchronic studies in rats, when extrapolated to humans and coupled with estimated exposure levels, suggest that the risk associated with dichlorobenzenes in the environment is not unreasonable.

The U.S. EPA has set the ambient water quality criterion for total dichlorobenzenes at 400 µg/l. This criterion is based on the highest long-term no-observed-effect level of 13.42 mg/kg/day reported for rats orally administered 1,2- or 1,4-dichlorobenzene for 5 to 7 months and a safety factor of 1000, placing the acceptable human intake at 0.94 mg/day. Exposure to the general population is well below this level. Inhalation appears to be the most significant route of exposure. Drinking water accounts for relatively low exposures, although heavily contaminatad drinking water in some local areas could possibly result in higher exposure levels. Risk to certain subpopulations exposed to local, elevated concentrations of dichlorobenzenes in air may occur through use of deodorizers or moth repellants containing 1,4-dichlorobenzene, or through proximity to industrial manufacturing or waste disposal sites. Exposure to these groups may approach 1 mg/day. Risk to occupationally exposed workers could be considerably higher than risk to the general population.

There are very few data available on either the effects or exposure of aquatic biota to dichlorobenzenes. Based on the monitoring data, there appear to be few reports of environmental concentrations of dichlorobenzenes at levels comparable to those causing adverse effects. In general, ambient and effluent concentrations are two orders of magnitude lower than effects levels. Aquatic biota may be at risk from accidental spilling or leakage of large quantities of the chemicals; in these cases, the duration of the exposure is expected to be short.

1.3 HUMAN EFFECTS AND EXPOSURE

The dichlorobenzenes are rapidly absorbed by humans via the lungs and gastrointestinal tract, and metabolized; they are also absorbed through the skin. The major target systems include the liver, the reticuloendothelial system, and the central nervous system.

Little specific information is available on the toxicity of dichlorobenzenes to humans. Anecdotal reports have linked chronic exposure to 1,2- or 1,4-dichlorobenzene with a few cases of human leukemia. A cause and effect relationship, however, cannot be reliably inferred from these reports. Occupational exposure to 1,4-dichlorobenzene suggests that no organic injury or adverse hematologic effects may be associated with air concentrations of 500 mg/m^3; concentrations greater than 960 mg/m^3 are intolerable, 400 mg/m^3 causes eye and nose irritation, and an odor is detectable at 90-180 mg/m^3. Exposure to concentrations up to 90 mg/m^3 of 1,2-dichlorobenzene caused no organic injury or adverse hematologic effects, while 300 mg/m^3 was detectable and 600 mg/m^3 produced irritation but no serious effects.

One study reported that there was no notable hazard due to skin irritation or dermal absorption of 1,4-dichlorobenzene, except under extreme conditions. A case of allergic purpura following 24-48 hour exposure to 1,4-dichlorobenzene and contact eczematoid dermatitis resulting from chronic skin exposure to 1,2-dichlorobenzene have been reported.

Existing health effects data from animal studies are limited. No long-term studies beyond 7 months' duration have been completed. Data from an ongoing study suggest that ingestion of 1,2-dichlorobenzene (86/mg/kg/day) does not induce oncogenic effects in either rats or mice, but the final decision on oncogenic potential should be deferred pending completion of the National Cancer Institute study. Mutagenic data for the dichlorobenzenes are inconclusive and limited to submammalian systems. Data on reproductive effects of the dichlorobenzenes are not available.

Although available health effects data are inadequate to characterize risk, sufficient subchronic data are available to estimate acceptable exposure levels. Inhalation of 560 mg/m^3 1,4-dichlorobenzene 7 hours/day, 5 days/week for 6-7 months showed no noticeable effects in a number of species of mammals. Oral LD$_{50}$ values for the dichlorobenzenes are generally in the 500 mg/kg range. The maximum tested oral dose of either 1,2- or 1,4-dichlorobenzene that produced no observed adverse effects in rats (13.42 mg/kg/day) was used by the EPA in establishing the water quality criterion. The Russian literature reports a maximum no-detected effect level in rats of 0.001 mg/kg/day. The reason for the discrepancy between these two levels is unclear; exposure levels and their determinations were not adequately addressed in the Russian literature.

Data on exposure to the dichlorobenzenes through ingestion are limited to those associated with consumption of drinking water. The maximum dichlorobenzene concentration observed in drinking waters was almost two orders of magnitude lower than the water quality criterion; the mean of observed values was lower by more than two orders of magnitude.

Human exposure to dichlorobenzenes through inhalation appears to be much larger than that through ingestion. The largest environmental releases are to the atmosphere, and estimated exposures through inhalation of ambient air range from 2 μg/day to 90 μg/day. The maximum value was reported for an urban location. Concentrations of dichlorobenzenes in air around industrial sites or disposal sites result in higher exposures to subpopulations living near these sources. Data from one study suggest that exposure associated with mothball usage (or possibly use of odor control agents) could reach 1 mg/day 1,4-dichlorobenzene for some people, but the extent to which these data are representative of widespread conditions remains to be confirmed. Occupational levels possess the potential for worker exposure significantly above that to the general population.

1.4 AQUATIC EFFECTS AND EXPOSURE

The lowest concentration of the dichlorobenzenes which was found to be toxic to marine and freshwater organisms was 1000 μg/l. The most sensitive species tested was the mysid shrimp with LC_{50}s of 1199-2850 μg/l. There was not a consistent difference in the level of toxicity observed for the three isomers, although Dalaemonetes pugio and Daphnia magna did show an increased sensitivity to the 1,2-dichlorobenzene isomer.

The concentrations reported for ambient and effluent waters are generally in the low ppb range (<10 μg/l); only one unremarked observation greater than 1000 μg/l was reported in STORET for ambient water and one for effluent water. Therefore, the exposure of biota to toxic levels in ambient waters can be assumed to be quite low. Results of the EXAMS model calculations suggest that removal of dichlorobenzenes from aquatic media is rapid; volatilization is the major removal mechanism in quiescent systems, whereas advection is much more effective in river systems. Fish kill data indicate that the accidental discharges of chemicals represent a source of possible exposure of aquatic biota to toxic concentrations of the dichlorobenzenes; the limited duration of the effects confirms the findings of EXAMS.

1.5 MATERIALS BALANCE

The total amount of dichlorobenzenes released to the environment in 1978 has been estimated to be approximately 13,500 kkg, more than one-half of the available U.S. supply (production minus exports plus imports). Environmental releases during production totaled 96 kkg to air, 6.3 kkg to land, and 230 kkg to water for 1,2-dichlorobenzene and 240 kkg to air, 7.7 kkg to land, and 290 kkg to water for 1,4-dichlorobenzene. These losses occur in vent gases; liquid waste streams from stills, wash tanks and strippers; and sludges. Inadvertent sources of dichlorobenzenes, such as industrial incineration and chlorination of drinking water, do not appear to release significant quantities to the environment.

In general, uses of the dichlorobenzenes are responsible for the major losses to the environment. Whereas manufacture accounts for only 2.8% of the environmental releases, use accounts for over 95%. The largest environmental releases are atmospheric. Emissions of 1,2-dichlorobenzene (≈ 5,500 kkg) occur primarily during solvent usage [e.g., cleaning or process solvents during toluene diisocyanate (TDI) or 3,4-dichloroaniline production] while the 1,4-isomer (≈ 24,000 kkg) is released as a result of use in mothballs and as a space deodorant. Most of these applications (except TDI process solvent use) represent widespread, dispersive uses, with the potential for exposure to the general public or specific population subgroups as a normal consequence of use.

Of the estimated 440 kkg dichlorobenzenes entering POTWs, calculations indicate that approximately one-half is lost to the air and one-half is discharged to water. The exact input of dichlorobenzenes to municipal incinerators is unknown, yet these compounds are probably destroyed with over 99.9% efficiency depending on conditions of temperature and residence time in the municipal facility. Dichlorobenzenes that are dispersed to landfills (520 kkg) arrive there primarily as garbage deodorants or as residue in used solvent containers.

1.6 ENVIRONMENTAL FATE

Most of the environmental discharges of dichlorobenzenes are released to the atmosphere; furthermore, the dichlorobenzenes released to aquatic systems are not expected to persist in the water column at high concentrations. The high vapor pressures and low water solubilities suggest that volatilization will be very important. Under experimental laboratory conditions, the half-life of 1,2-dichlorobenzene, as a function of volatilization, was estimated to range from 1.6 to 6.7 hours, depending on the current and wind velocities of the system. The octanol:water partition coefficient suggests that adsorption onto soils and sediments will also be a major pathway for removal from the water column. The rate of biodegradation in the environment may also be sufficiently high that biodegradation would be a major fate process.

Results of the Mackay equilibrium partitioning model for 1,2-dichlorobenzene indicate that in a system at equilibrium, 35% of the chemical will be in the air compartment, 64% in the sediment, and 0.3% in the water column. Aquatic fate was also modelled by use of EXAMS, which incorporates some of the other fate processes to give a more complete estimate of the behavior of the dichlorobenzenes in environmental systems. Three generalized aquatic systems were modelled in EXAMS: a pond, an oligotrophic lake, and a river system.

In the pond, 84% of the 1,2-dichlorobenzene is expected to be in the sediment at steady state; volatilization will be the major removal process from water. Following suspension of the loading (1 kg/hour), 33% of the 1,2-dichlorobenzene in the system will be removed within 24 days. In an oligotrophic lake, most of the chemical will reside in the water column, where it will be subject to rapid volatilization. Within 24 days of cessation of the loading, results of the EXAMS run predict that 66% of the

1,2-dichlorobenzene will have been removed from the system. Finally, EXAMS was used to model the river system, the system most likely to receive discharge of dichlorobenzene from an industrial source or from accidental spills or leakage. In the river system, at steady-state, the chemical is expected to be distributed between the water and sediment compartments as follows: 75% in water, 25% in sediment. Volatilization is not the predominant removal process in a dynamic system such as the river where other processes (such as advection) are more important. After cessation of the 1 kg/hour loading, 76% of the 1,2-dichlorobenzene will be removed from the system within 12 hours; 99.9% of the dissolved chemical will be lost from the water, 2.33% removed from the sediment. These environmental fate data support the observation that discharges of dichlorobenzenes (to river systems) that were responsible for large fish kills affected the biota for periods of only 1 day; the levels would have been substantially diminished in less than 12 hours.

Monitoring data for the dichlorobenzenes are quite limited. Ambient and effluent dichlorobenzene concentrations reported in the STORET data base were generally less than 10 μg/l. However, most of the data were remarked, and the discussion is largely of detection limits. Drinking water data indicated maximum levels less than 10 μg/l.

Air monitoring data indicate ambient levels of dichlorobenzenes generally below 1 $\mu g/m^3$. A Japanese study reported urban concentrations up to 4.2 $\mu g/m^3$ and suburban concentrations up to 2.4 $\mu g/m^3$. Ambient air near industrial or disposal sites in the U.S. was reported to contain up to 46 $\mu g/m^3$ of total dichlorobenzenes. Room concentrations associated with mothball usage were measured at 105 $\mu g/m^3$.

2.0 INTRODUCTION

The Office of Water Regulations and Standards, Monitoring and Data Support Division, the U.S. Environmental Protection Agency, is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and estimate the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing a suitable regulatory strategy for reducing the risk if such action is indicated.

This report on the dichlorobenzenes includes separate discussions of the three isomers whenever practical. The isomeric designations used are 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene; ortho-, meta- and para-dichlorobenzene are common alternative designations for the three isomers. The 1,2- and 1,4-dichlorobenzene isomers are the only ones produced and used in significant quantities. Most of the data on exposure and effects are specific to these two isomers so they are dealt with in more detail in the following chapters. However, there are limited monitoring data for all three isomers. The physiochemical data indicate that they are similar, but in making a risk assessment, each should be considered a separate chemical.

This document is an assessment of the risks associated with exposure to the dichlorobenzenes. Information on production, use, fate and distribution of these chemicals is included in order to determine the exposure associated with specific activities. The report is organized as follows:

- Chapter 3.0 presents a materials balance for the dichlorobenzenes that considers quantities of the chemical consumed or produced in various processes, the amount of pollutant released to the environment, the environmental compartment intially receiving it, and, to the degree possible, the locations and timing of releases.

- Chapter 4.0 describes the distribution of the dichlorobenzenes in the environment by presenting available monitoring data for various media and by considering the physiochemical and biological fate processes that transform or transport the chemicals.

- Chapter 5.0 discusses the available data concerning the toxicity of the dichlorobenzenes for humans and laboratory animals and quantifies the likely level of human exposure via major known exposure routes.

- Chapter 6.0 presents the reported effects levels and estimated exposure levels for aquatic biota.
- Chapter 7.0 compares exposure conditions for humans and other biota with the available data on effects levels from Chapters 5.0 and 6.0. The risks associated with various exposures to the dichlorobenzenes are discussed.
- Appendices A and B provide supporting information for Chapter 3.0.

3.0 MATERIALS BALANCE

3.1 INTRODUCTION

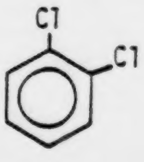
One perspective from which exposure to a chemical may be evaluated is that of a materials balance. Since the total mass of all materials entering a system equals the total mass of all materials leaving that system, excluding those materials the system accumulates or retains, a materials balance may be performed around any individual operation that may ultimately place a specific population at risk. (e.g., process water discharges creating groundwater contamination). Each overall materials balance, therefore, consists of a collection of smaller scale ones, each of which is directed to specific releases to the environment. It is beyond the scope of this chapter to predict the fate of the chemical following release.

The chapter reviews both published and unpublished data concerning the production, use, and disposal of dichlorobenzenes within the United States. Information from the available literature has been critiqued and compiled to present an overview of major sources of environmental release of dichlorobenzenes. Fully annotated tables have been included to aid data evaluation. Since a negligible amount of 1,3-dichlorobenzene is manufactured in this country, the major emphasis of this chapter is on the distribution of releases of 1,2- and 1,4-dichlorobenzenes.

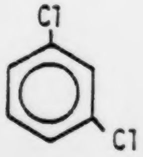
Section 3.2 discusses the production of 1,2-dichlorobenzene and 1,4-dichlorobenzene; 1,3-dichlorobenzene is not produced in significant quantities, and is not discussed in detail. The numerous uses of the dichlorobenzenes and the attendant environmental releases are reviewed in Section 3.3. Section 3.4 presents a discussion of the disposition of dichlorobenzenes discharged to municipal waste facilities, i.e., publicly-owned treatment works (POTWs) and urban refuse landfills or incinerators. A materials balance flow sheet for the dichlorobenzenes and a summary of the major findings are presented in Section 3.5.

3.2 PRODUCTION OF DICHLOROBENZENES

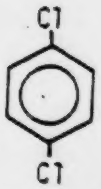
The three dichlorobenzene isomers are shown below:



1,2-dichlorobenzene
ortho-dichlorobenzene
o-dichlorobenzene



1,3-dichlorobenzene
meta-dichlorobenzene
m-dichlorobenzene



1,4-dichlorobenzene
para-dichlorobenzene
p-dichlorobenzene

This section describes the manufacture of dichlorobenzenes. In addition, environmental releases from manufacture are estimated using available data, and the possible inadvertent sources of dichlorobenzene release to the environment are discussed.

3.2.1 Manufacture

3.2.1.1 Overview

The 1978 production figures for 1,2- and 1,4-dichlorobenzenes were available from two sources: U.S. International Trade Commission (USITC) and an employee exposure report by Hull and Company (Hull 1980). The two production totals differ considerably: 38,000 kkg were reported by USITC and 60,000 kkg by Hull and Co. The data from the latter were chosen for use in this materials balance because they were the result of direct industry contacts. In addition, there apparently was a reporting error in production figures by one company to USITC (Hull 1980). (The identity of this facility could not be revealed for proprietary reasons.) Table 3-1 summarizes location, production, and environmental release data for 1,2- and 1,4-dichlorobenzene manufacture. The third isomer, 1,3-dichlorobenzene, is not produced in significant quantities, although it has many potential uses (EPA, 1979d; see Sections 3.2.1.4 and 3.5).

Historically, 1,2- and 1,4-dichlorobenzene were produced largely as byproducts of monochlorobenzene manufacture. However, demand for monochlorobenzene has dropped in the last decade. In the future, therefore, production facilities are expected to be shifted toward maximizing the yield of dichlorobenzenes (EPA 1978a, Mannsville Chemical Products 1978, Lewis 1975).

Chlorobenzenes are produced by direct chlorination of benzenes in continuous or batch reactors. A combination process may be used in which batch chlorination is followed by continuous product refining (SRI 1979b). The product is a mixture of monochlorobenzene and 1,2- and 1,4-dichlorobenzenes as major products, along with small amounts of higher chlorinated benzenes (Kurtz and Smalley 1979). The major reactions are:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

$$C_6H_5Cl + Cl_2 \longrightarrow C_6H_4Cl_2 + HCl$$

The HCl product, contaminated with benzene and chlorinated products, passes overhead. The reactor bottoms are scrubbed with benzene or chlorobenzenes and passed to a neutralizer where they are washed with aqueous sodium hydroxide to remove HCl and most of the dichlorobenzenes, thus forming a sludge and a supernatant. The sludge, rich in dichlorobenzenes, is distilled into 1-4- and 1,2- fractions. The supernatant is also distilled, to separate benzene, monochlorobenzene, and 1,2- and 1,4-dichlorobenzenes (Lowenheim and Moran 1975).

Table 3-1. Dichlorobenzene Materials Balance: Production, 1978(kkg/yr)[a]

Producers and Location[b]	Capacity[b]	Production[c]	Environmental Releases[d]		
			Air[e]	Water[f]	Land[g]
1,2-Dichlorobenzene					
Allied Chemical Corp. Syracuse, NY	1,800	770	2.7	6.6	neg[h]
Dow Chemical Corp. Midland, MI	14,000	6,000	21	51	1.4
Monsanto Company Sauget, IL	7,300	3,100	11	26	neg
PPG Industries, Inc. Natrium, WV	9,100	3,900	14	33	neg
Specialty Organics, Inc. Irwindale, CA	910	390	1.4	3.3	neg
Standard Chlorine Chemicals Co. Inc.					
Delaware City, DE	23,000	9,800	35	84	2.3
Kearny, NJ	7,300	3,100	11	26	neg
Totals	63,000	27,000	96	230	6.3
1,4-Dichlorobenzene					
Allied Chemical Corp. Syracuse, NY	1,800	770	5.6	6.8	neg
Dow Chemical Corp. Midland, MI	14,000	6,000	43	53	1.4
Monsanto Company Sauget, IL	5,500	2,400	17	21	neg
PPG Industries, Inc. Natrium, WV	14,000	6,000	43	53	1.4
Specialty Organics, Inc. Irwindale, CA	910	390	2.8	3.4	neg
Standard Chlorine Chemicals Co. Inc.					
Delaware City, DE	34,000	15,000	110	130	3.5
Kearny, NJ	6,800	2,900	21	26	neg
Totals	77,000	33,000	240	290	7.7

a) All values rounded to two significant figures.

b) SRI, 1979b.

c) Total production: Hull, 1980. Breakdown by plant based on plant capacity.

d) Environmental releases distributed based on plant capacity.

e) See Table A-1 (Appendix A) for emission factors; emissions distributed as process (65%), storage (13%), fugitive (21%).

f) Based on 0.0037 kg dichlorobenzenes/kg monochlorobenzene produced, in water stream from dichlorobenzene column; 1.4 x 10^5 kkg monochlorobenzene produced, 1978; proportion which is each isomer is based on production.

g) Based on 0.0001 kg dichlorobenzenes/kg monochlorobenzene produced, land disposed from fractionating towers; Hull, 1980; EPA, 1977c.

h) Negligible; <1 kkg.

3.2.1.2 Batch Chlorination

In the batch chlorination process (see Figure A-1, Appendix A,) chlorine is bubbled into a reactor charged with benzene at a rate that maintains a temperature of 40° to 60°C (Lowenheim and Moran 1975). The top and bottom streams are treated as described above. At 100% chlorination, the yield is about 80% monochlorobenzene, 15% 1,4- and 5% 1,2-dichlorobenzene, with insignificant amounts of higher chlorinated benzenes (Kurtz and Smalley 1979). The 1,2-dichlorobenzene is separated from the 1,4- isomer by washing the 1,4-dichlorobenzene crystals with methanol and heating at 100°C under vacuum (EPA 1977b). Two or three kg of 1,4-dichlorobenzene are formed per kg of 1,2-dichlorobenzene (SRI 1979a). For high yields of 1,4-dichlorobenzene, either an aluminum chloride catalyst is used or the mixed product stream is further chlorinated to convert 1,2-dichlorobenzene to trichlorobenzene, with subsequent fractional distillation of 1,4-dichlorobenzene from the remaining chlorobenzenes (Catalytic 1979).

3.2.1.3 Continuous Chlorination

Continuous chlorination is used to minimize the production of higher chlorinated products, including the dichlorobenzenes (Lowenheim and Moran 1975; see Figure A-2, Appendix A). The reaction takes place in a series of combined chlorination-fractionation chambers. The partially chlorinated material is sent to a distillation unit, where the benzene is distilled and returned to the chlorinator. Hydrogen chloride is then passed through one or more towers in which the high boiling chlorobenzenes are used to remove organic contaminants. The hydrogen chloride may be recovered as either an anhydrous product or aqueous solution, with a carbon column being used if flow organic specification is required. The other chlorinated products are further fractionated into heavy tars (mostly dichlorobenzenes) and monochlorobenzene, which is neutralized as in batch chlorination (Lowenheim and Moran 1975). Thus, monochlorobenzene is immediately isolated and only fresh benzene is exposed to chlorine (EPA 1975a), with a resultant yield of up to 95% monochlorobenzene (EPA 1977a).

3.2.1.4 1,3-Dichlorobenzene

This isomer is not produced in commercially significant quantities by direct chlorination (EPA 1977d). Alternative methods that have been proposed include hydrogenolysis of trichlorobenzenes (Crowder and Gilbert 1958, Redman and Weimer 1960) and dechlorination of hexachlorocyclohexane (lindane) (Allirot 1972). The usual method is isomerization of 1,2- and 1,4-dichlorobenzenes (EPA 1977d), generally at high temperature and pressure (EPA 1977a, Pray 1958). Various patents relating to 1,3-dichlorobenzene manufacture are shown in Table A-2, Appendix A.

3.2.1.5 Environmental Releases

Releases of the dichlorobenzenes occur at many stages during manufacture, in vent gases, liquid waste streams, or sludges. Table 3-1 shows calculated losses from production. Very low air emissions of dichlorobenzenes occur through vents on the tail gas absorber, as by-product HCl is essentially free of organic compounds (Lewis 1975). Overall emissions have been reported as 3.55 kg 1,2-dichlorobenzene lost/kkg produced and 7.24 kg 1,4-dichlorobenzene lost/kkg produced (EPA 1980e). The resultant 96 kkg and 240 kkg air emissions of the respective isomers, subdivided into process, storage, and fugitive losses, are distributed by individual plants, based on capacity, as shown in Table 3-1.

Because 1,4-dichlorobenzene sublimes at room temperature, further air emissions may eventually be expected from liquid and solid waste streams (EPA 1979b). Liquid waste is discharged from stills, wash tanks, and strippers involved in product refining (Catalytic 1979). For the batch process, discharges from the dichlorobenzene column wash stream have been estimated as 0.0037 kg/kg monochlorobenzene produced (EPA 1975a). Based on 1.4 x 10^5 kkg monochlorobenzene produced, 290 kkg of 1,4-dichlorobenzene are released to water, along with 230 kkg 1,2-dichlorobenzene (see Table 3-1).

Dichlorobenzene releases in 1,2-dichlorobenzene column waste have been estimated as 0.0001 kg/kg monochlorobenzene produced (EPA 1975a). This amounts to 14 kkg of dichlorobenzenes discharged to land. In addition, 0.044 kg of "polychlorinated aromatic resinous" sludge of indeterminate composition is released per kg monochlorobenzene produced (EPA 1975a), totalling 6,200 kkg in 1978. As this sludge, discharged to industrial and sanitary landfills, is rich in dichlorobenzenes and is the major source of pollutant discharge (EPA 1979a), a much larger amount than 14 kkg of dichlorobenzenes could be disposed of on land.

It is relevant to note that Brown et al. (1975, as cited in EPA 1977a) have estimated losses to the environment (410 kkg 1,2-dichlorobenzene and 540 kkg 1,4-dichlorobenzene) similar to the 330 kkg 1,2-dichlorobenzene and 540 kkg 1,4-dichlorobenzene calculated as released to all media in this materials balance. Another document estimated total losses of dichlorobenzenes during production of monochlorobenzene as 2,900 kkg to water and 3,100 kkg to land (EPA 1978b), but no rationale was provided for these estimates.

3.2.2 Inadvertent Sources of Dichlorobenzene

Any human activity that unintentionally generates a chemical and disperses it to the environment may be called an "inadvertent source" of that chemical. The following considerations indicate that inadvertant sources do not appear to contribute significant amounts of dichlorobenzenes to the environment. Disposal per se (e.g., POTWs and Urban Refuse) is discussed in Section 3.4.

While chemical plants are often inadvertent sources of chemicals due to production of byproducts, in this case these routes have been considered in discussions of the production processes (Section 3.2.1.5). Disinfection of drinking water or wastewater by chlorination is another potentially important inadvertent source of chlorinated hydrocarbons (see Section 3.4, Municipal Disposal of Dichlorobenzenes). Contamination of municipal drinking waters has also been investigated in the National Organic Monitoring Survey (NOMS), which examined 113 community water supplies, representing all types of sources and treatment processes, in three phases during a twelve month period (EPA, 1977f). As shown in Appendix A (see Table A-3), dichlorobenzenes are detected neither frequently nor in high concentration. Moreover, the source of dichlorobenzenes, when they were found, is not readily apparent, though the data suggest that chlorination is not a significant source of dichlorobenzenes found in these waters. A similar conclusion can be derived from another study that found the highest levels of 1,2-, 1,4-, and 1,3-dichlorobenzenes in drinking water to be only 1, 1, and <3 µg/1, respectively (EPA, 1975b, see Table A-4, Appendix A).

EPA has summarized data on two other inadvertent sources, coal mining and iron/steel manufacturing. The latter industry appears to be the only source of significant loading, approximately 4 kkg of 1,4-dichlorobenzene per year in treated wastewater (EPA 1980f).

A final possible inadvertent source of dichlorobenzenes released to the environment may be the incineration of polyvinyl chloride (PVC) materials. A pilot-scale study on combustion of PVC at temperatures between 570° and 1100°C at various residence times and excess air levels indicated emission factors of 0.10 mg to 22 mg of dichlorobenzene(s) per kg of PVC burned (Ahling et al. 1978). The published data do not show any consistent correlation between emission levels and combustion conditions, so estimation of the significance of this possible source of dichlorobenzene emissions is difficult to make at this time. Nonetheless, it should be noted that this source may be increasingly important as incineration competes with land disposal for municipal waste treatment.

An unresolved question at the present time is whether there are any identifiable inadvertent sources of 1,3-dichlorobenzene. Monitoring data (Section 3.4.1) suggest that this isomer may be present in the environment at levels that are comparable to the 1,2- and 1,4- species, while the materials balance analysis indicates production and use of 1,3-dichlorobenzene to be at least three orders of magnitude lower than 1,2- and 1,4-dichlorobenzene.

3.3 USES OF DICHLOROBENZENES

3.3.1 Overview

The uses of dichlorobenzenes can be divided into the following three major categories: (1) use as a reactant in chemical synthesis, (2) use as a process solvent, and (3) use as a formulation solvent. For the first two applications, the shipping destination represents the point of most likely release to the environment. Release of dichlorobenzene used as a formulation solvent, however, can occur prior to, during and after the manufacturing process of formulation.

This section will examine the variety of specific uses of dichlorobenzenes, from mothballs to solvent uses and dye synthesis. The 1,2- and 1,4- isomers account for essentially 100% of the dichlorobenzene used. Although 1,3-dichlorobenzene has a number of potential uses, negligible commercial production is reported (Kao and Poffenberger 1979); therefore, this isomer is considered to have an insignificant impact on the overall materials balance. A summary materials balance for the total use categories is presented in Table 3-2, which includes the limited quantitative data available on environmental releases of the isomers discussed below. A table showing the frequency of dichlorobenzene detection in various industrial wastewater streams has been included in Appendix B (see Table B-1).

3.3.2. 1,2-Dichlorobenzene

3.3.2.1. Overview

Total U.S. production of 1,2-dichlorobenzene in 1978 was estimated to be 27,000 kkg (Hull 1980). While 3,200 kkg of this material were exported that year, 210 kkg were also imported, for a net domestic supply of about 24,000 kkg (U.S. Dept. of Commerce 1980, SRI 1979a).

It is estimated that the 1,2-dichlorobenzene domestic supply in 1978 was distributed as follows: 70% to organic synthesis (primarily 3,4-dichloroaniline); 15% to toluene diisocyanate manufacture as a process solvent; 8% to miscellaneous formulated solvent uses; 4% to dye manufacture and application; and 4% to other minor uses, primarily pesticides manufacture (SRI 1979a). The following is a discussion of the major uses (the minor uses will be covered together with 1,4-dichlorobenzene minor uses in Section 3.3.4).

Table 3-2. Dichlorobenzene Materials Balance: Use, 1978 (kkg/yr)[a]

Isomer	Use Category	Consumption[b]	Contained in Products	Environmental Releases		
				Air	Land	Water
1,2-Dichlorobenzene	Synthesis of 3,4-Dichloroaniline	17,000	17,000	24[c]		
	Toluene Diisocyanate Manufacture	3,600		3,600[d]	neg[d]	
	Miscellaneous Solvents	1,900		1,900[e]	20[e]	12[e]
	Dye Manufacture	960	960	neg[c]		
	Others[f]	720	650	70[f]		
	Exports	3,200[g]				
	Imports		210[g]			
1,3-Dichlorobenzene		neg				
1,4-Dichlorobenzene	Space Deodorant	15,000		14,000[h]	500[h]	500[h]
	Moth Control	9,500		9,500[i]	1[i]	1[i]
	Other[j]	2,700	2,700	5[j]		
	Exports	6,300[g]				
	Imports		430[g]			

a) Numbers may not add due to rounding to two significant figures.

b) Input figures: Hull, 1980 (total); SRI, 1979a (percentage breakdown).

c) See Table A-1 (Appendix A) for emission factor; negligible: <1 kkg.

d) Air: all assumed released to the atmosphere, EPA, 1980e; Land: 558 kkg residue/TDI plant/yr, 100 ppm ortho-dichlorobenzene in residue (nine plants) EPA, 1977a/b; Lewis, 1975.

e) Cleaning solvents: 99% released to air, 1% to land with containers, Simmons, 1980. Discharge of 12 kkg is from dye carrier use (see Section 3.4.1.4).

f) Partial survey of users for odor control in sewage: 70 kkg, Hull, 1980; 100% lost to the atmosphere. Negligible (<1 kkg) loss from pesticide manufacture (see Table 3-3). Indeterminate amount used for agricultural chemicals and laboratory supply.

g) U.S. Dept. of Commerce, 1980; SRI, 1979a. Placement of imports and exports in respective columns are for purposes of materials balance, not to imply that each goes solely to containment in a product or a specific use.

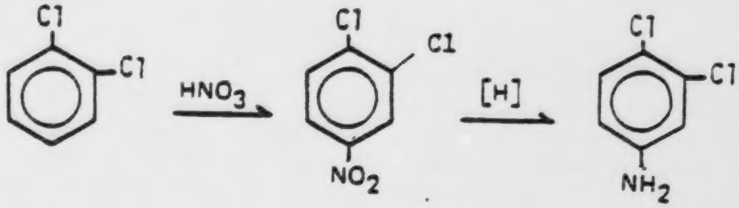
h) 90% released to air, 10% to either water (toilet deodorizer) or land (garbage deodorizer), Willert, 1980.

i) All domestically-used mothballs assumed to release para-dichlorobenzene to the atmosphere during use. Environmental releases also include use in textile mills (see Section 3.4.1.4).

j) Primarily pesticide manufacture (see Table 3-3 for emissions), plus: dye synthesis, abrasives, floor waxes and finishes, and agricultural chemicals, SRI, 1979a; Hull, 1980.

3.3.2.2 Synthesis of 3,4-Dichloroaniline

The primary use of 1,2-dichlorobenzene, amounting to 17,000 kkg in 1978 (SRI 1979a), is the synthesis of 3,4-dichloronitrobenzene, which is subsequently reduced to 3,4-dichloroaniline by the following reactions:



This white, crystalline end product is used chiefly to manufacture urea herbicides, the most important of which is propanil, a rice herbicide (SRI 1979a). It also has minor applications in pesticides, bactericides, and dyestuffs. The reaction step utilizing 1,2-dichlorobenzene is a captive one, with most of the dichlorobenzene claimed to be either consumed, recovered, or recycled (Zeftel 1980). The producers of 3,4-dichloroaniline, along with data on 1,2-dichlorobenzene emissions, are listed in Table B-2.

3.3.2.3 Manufacture of Toluene Diisocyanate

The manufacture of toluene diisocyanate (TDI) consumes 15% or 3,600 kkg of the net 1,2-dichlorobenzene domestic supply (SRI 1979a). Toluene diisocyanate is used in urethane polymers, primarily for flexible foams in furniture cushions. The producers of toluene diisocyanate, plant capacities, and 1,2-dichlorobenzene emissions are presented in Table B-3.

As shown schematically in Figure B-1, 1,2-dichlorobenzene is used as a process solvent in which diaminotoluene is dissolved prior to reaction with phosgene to produce crude toluene diisocyanate. The 1,2-dichlorobenzene is recovered during distillation of unreacted phosgene (which the solvent has absorbed) and during vacuum distillation of the crude toluene diisocyanate. Although no specific data on emissions were available, it has been estimated that virtually all (3,600 kkg) of the 1,2-dichlorobenzene utilized for TDI manufacture is eventually released to the atmosphere (EPA 1980e), through vents, scrubbers and leaking valves or pipes (see Table B-3). The distillation residue is incinerated (Chadwick and Hardy 1967, Sato 1966) or often disposed of on land (EPA 1977a). It has been estimated that 558 kkg of centrifuge residue are produced per toluene diisocyanate plant per year from evaporator units for TDI purification and solvent recovery, and that this residue contains no more than a few hundred ppm 1,2-dichlorobenzene (EPA 1977a, EPA 1977b, Lewis 1975). If the 1,2-dichlorobenzene concentration in the residue is 100 mg/kg, a total of <1 kkg should be discharged to land from the nine plants producing toluene diisocyanate.

3.3.2.4 Miscellaneous Solvent Uses

As is the case for many chlorinated hydrocarbons, 1,2-dichlorobenzene exhibits useful solvent properties which give it a wide range of applications. An estimated 8% or 1,900 kkg of the annual 1,2-dichlorobenzene net supply is consumed in the solvent market, which includes automobile engine cleaners, fuel additives, and carburetor cleaners.

The 1,2-dichlorobenzene isomer is also used as a solvent in paint formulations, as well as in compounds for removing paints, inks, varnishes, lacquers, resins, gums, waxes, heavy greases, acetylcellulose, sulfur, organic sulfur compounds and oxides of nonferrous metals. In addition, 1,2-dichlorobenzene is a very good solvent for rubber and tar, and is frequently used to remove tarry residues in stills and other processing equipment. Other solvent applications include: shoe polish, metal polish, firearms, cleaners, rust preventatives, and other cleaning/polishing formulations, dissolving pitch on papermaking felts, degreasing leather hides/woolen pelts, and as a carrier solvent for preservatives/repellents in wood-preserving compounds (SRI 1979a, Zacharias, 1980, Hull 1980, PPG, 1977).

In this study, all of the 1,2-dichlorobenzene used in miscellaneous solvents is assumed to be discharged to the environment, due to the number of small operations performed and the attendant economic infeasibility of solvent recovery. Furthermore, 99% of the emissions (1,880 kkg) are estimated to be released to the air, with the remaining 1% (20 kkg) discharged to land in containers (Simmons 1980; see Table 3-2).

3.3.2.5 Dyes: Synthesis and Application

The compound 1,2-dichlorobenzene serves a dual purpose in the dye industry, in both manufacture and application of the dyestuffs. Approximately 3% or 960 kkg of the net 1,2-dichlorobenzene supply is used as a dye carrier, or as a process solvent or reactive intermediate in dye synthesis (SRI 1979a).

Dye carriers, also called dye accelerants, are used to achieve complete dye penetration of synthetic fibers, primarily polyester. The carriers effectively loosen the interpolymer bonds of the fibers to allow penetration of disperse dyes. (Disperse dyes are water-insoluble, nonionic dyes for application to hydrophobic fibers from an aqueous suspension.) This process is not needed for natural textiles since they contain open, partially hollow structures, which are easily penetrable by dyes.

Dying procedures vary according to the makeup of the textile material. Almost all 100% polyester is pressure dyed, utilizing an average of 2% by weight dye carrier to fabric. An atmospheric process is used for blended materials (less than 100% polyester) and requires a higher concentration of dye carrier, an average of 10% by weight (Stone 1980). No exact figure is available for 1,2-dichlorobenzene release from consumption as a dye carrier, but the compound does find widespread use in this market [BASF Corporation, however, reports that a mixture of isomers acts as a better carrier (Seizenger 1980)]. It seems probable that all of the dichlorobenzene used annually as a dye carrier is eventually released into the environment. (A possible scheme for control of dichlorobenzene release from use as a dye carrier is shown in Figure B-2.)

Contradictory information has been received on one use of 1,2-dichlorobenzene. Some references discuss the use of 1,2-dichlorobenzene as a dye intermediate (EPA 1977c, Bannister et al. 1979), but industry representatives claim that use of the dichlorobenzenes is limited to the role of process solvent rather than as reactive precursors (Lonenzo 1980, Anderson 1980). Nonetheless, PPG Industries, Inc. does mention the sulfonation of 1,2-dichlorobenzene to produce the dyestuff 3,4-dichlorobenzene-sulfonic acid (PPG 1977) and the manufacture of 3,4-dichloroaniline, sometimes used as a dyestuff, has already been discussed (see Section 3.3.2.2). Specific dyes for which 1,3-dichlorobenzene use as a process solvent during production has been documented are listed in Table B-4, along with the names and locations of the dye manufacturing plants. Dichlorobenzene used as a process solvent may conservatively be assumed to be released to the environment in amounts equal to the annual usage for this application. The releases to water, land, and air can be estimated as described below.

Environmental release data for the dye industry are limited. Levels of up to 380 μg/l dichlorobenzene in raw wastewater and 32 μg/l in final effluent have been found in one dye manufacturing plant (Games and Hites 1977), but a total flow for the entire industry is not presently available. Analysis of wastewater samples from textile mills, where 1,2-dichlorobenzene might be used as a dye carrier, revealed a maximum level of 290 μg/l of 1,2-dichlorobenzene in raw wastewater and 20 μg/l in the treated water (EPA, 1980f). Using a total annual wastewater volume of 600 x 10^6 m^3/yr (EPA, 1976b), a total release of 12 kkg is estimated for treated effluent from this industry. Releases of dichlorobenzene to land and air may be estimated from the difference between these concentrations in raw and treated wastewater and total industry flow and by use of the assumption that the material removed from the water is either incorporated in or absorbed onto sludge destined for land disposal, or volatilized to the atmosphere. The resultant total is 160 kkg of 1,2-dichlorobenzene. The data describing the behavior of dichlorobenzenes in publicly-owned treatment works (POTWs; see Section 3.4., Table 3-4) can serve as a basis for assuming that 99% of this latter amount will end up in the air and only 1% in sludge (see Table 3-2). A similar calculation for 1,4-dichlorobenzene, using concentrations of 220 μg/l for raw and 1.5 μg/l for treated wastewater (EPA 1980f), gives an estimate of 0.9 kkg of water, 130 kkg to air, and 1.3 kkg to land (see Table 3-2).

This isomer is used for moth-proofing of textiles (see Section 3.3.3.3) and could possibly be an ingredient or impurity in some dye carriers (EPA 1979b). These releases are included in the emissions reported for use of 1,4-dichlorobenzene for moth control.

3.3.3 1,4-Dichlorobenzene

3.3.3.1 Overview

In 1978, 33,000 kkg 1,4-dichlorobenzene were produced, 6,300 kkg exported and 430 imported (Hull 1980, U.S. Dept. of Commerce 1980). As in most years, a significant percentage of the 27,000 kkg 1,4-dichlorobenzene remaining for domestic consumption was formulated into blocks, balls, and cakes, devoted to space deodorants (55%) and moth control (35%); the remaining 10% was comprised of minor uses (SRI 1979a). This section discusses the two major uses of 1,4-dichlorobenzene, while the minor uses will be covered along with those of 1,2-dichlorobenzene in Section 3.3.4.

3.3.2.2 Odor Control

Space deodorizing is the largest volume market for 1,4-dichlorobenzene, accounting for 55% (15,000 kkg) of the net domestic supply in 1978 (SRI 1979). This category includes deodorants for toilet bowls, urinals, garbage and diaper pails (EPA 1977a). These products are usually sold as 100% 1,4-dichlorobenzene blocks, although perfume is often added. The predominant approach in public urinals has been to use odor-masking agents, but a recent study has investigated the use of a urease/1,4-dichlorobenzene composition to control the source of odor, as well as alleviate odor (Weber 1977).

Of the 15,000 kkg of 1,4-dichlorobenzene used in the category, all is assumed to be released to the environment, by sublimation to the atmosphere, flushing into sewers or land disposal with garbage. It is estimated that approximately 90% (14,000 kkg) of the 1,4-dichlorobenzene used for this purpose is released to the air; the remaining 10% (1,000 kkg) is released to either land or water, depending upon whether it is used as a garbage deodorant or toilet deodorant, respectively (Willert 1980).

3.3.3.3 Moth Repellant

The 1,4- isomer has been used extensively in household mothballs for many years. In 1978, this use consumed 9,500 kkg (35%) of the 1,4-dichlorobenzene available for domestic consumption (SRI 1979a, see Table 3-2). With the increased use of synthetic fabrics, the market for mothballs should decline.

Numerous brands of mothballs are available to the consumer, containing $\geq$99% 1,4-dichlorobenzene (EPA 1980d). Other examples of moth/

insect control with 1,4-dichlorobenzene include preservation of glycerin-treated dried flowers during shipment, moving and storage (vans and warehouses), mothproofing of textiles during production, and possible use by furriers (Hull 1980, EPA 1979b). For the purpose of this materials balance, essentially all of the 1,4-dichlorobenzene used in mothballs is assumed to be released to the atmosphere, with approximately 1 kkg going to water and land from the textile industry (see Section 3.3.2.5). Morita and Ohi (1975) found the following 1,4-dichlorobenzene levels in indoor air: inside wardrobe, 1,700 $\mu g/m^3$; inside closet, 315 $\mu g/m^3$; bedroom, 105 $\mu g/m^3$ (see Table B-5).

3.3.4 Minor Uses

3.3.4.1 Overview

The minor uses of 1,2- and 1,4-dichlorobenzene, though comprising only a small percentage of total output, totalled approximately 3,400 kkg in 1978. These uses include: agricultural chemicals, abrasives, odor control, laboratory applications, dye synthesis (1,4-dichlorobenzene), and uses in various other formulated products. The miscellaneous uses in this category (those other than pesticide manufacture) are generally dispersive in nature (i.e., exposure results as a normal consequence of use). Therefore, the small volume involved belies the fact that the potential for high exposure levels to a specific consumer population could exist.

3.3.4.2 Agricultural Chemicals

Both 1,2- and 1,4-dichlorobenzene are listed in the Farm Chemicals Handbook (1975) for various applications in the agricultural chemicals industry. In addition, EPA's Pesticides Division maintains a list of products that contain either of the two isomers (EPA 1980d). Estimates of emissions from pesticide manufacture, distributed by geographic region, are presented in Table 3-3.

Besides moth control, discussed in Section 3.3.3.3, 1,4-dichlorobenzene can also be applied to tobacco seed beds for blue mold control, for control of peach tree borers, and to combat mildew and mold on leather and fabrics. The 1,2-dichlorobenzene isomer possesses a slightly wider range of applications, including use as an herbicide, insecticide, and soil fumigant. It has been used to control mites, termites, peach tree borers, bark bettles and grubs, as well as insects and mites in poultry houses and animal sleeping quarters (Farm Chemicals Handbook 1975).

The exact amount of each isomer devoted to agricultural chemicals was not available (see Table 3-2). Nonetheless, it is assumed that a large portion of the amount used for this purpose is released to the atmosphere.

Table 3-3. 1978 Dichlorobenzene Emission Estimates from Pesticide Manaufacturers[a]

Region	Number of Sites per Region	1,2 -dichlorobenzene Emissions (kg/yr)[b]	1,4 -dichlorobenzene Emissions (kg/yr)[c]
New England	4	10	40
Middle Atlantic	37	96	370
East North Central	19	49	190
West North Central	15	39	150
South Atlantic	17	44	170
East South Central	14	36	140
West South Central	15	39	150
Mountain	5	13	50
Pacific	13	34	130
Total	139	360	1,400

a) Values rounded to two significant figures.
b) Average per site 2.6 kg/yr; see Table A-1 for emission factor.
c) Average per site 10 kg/yr; see Table A-1 for emission factor.

Source: EPA, 1980e.

3.3.4.3 Abrasives Manufacture

A minor application of 1,4-dichlorobenzene, probably accounting for <1 kkg annually (Richards 1980), is its use in the manufacture of abrasive grinding wheels. Production involves the bonding of abrasive grains (i.e., aluminum oxide, silicon carbide, diamond) to the wheel shape, using a ceramic (vitrified) or resin (resinoid) matrix. The 1,4-isomer (as well as naphthalene) is used as an additive in the grain and bond mixture to faciliate a more open spacing of the grains. The additive vaporizes during the curing operations. The compound is well-suited for this application, due to its hard crystalline nature, ability to be crushed to definable grit sizes, and quick vaporization at the curing temperatures (1,200°C for the vitrified matrix and 150-200°C for the resinoid matrix).

Although reference is made to the use of 1,4-dichlorobenzene in resinoid-bonded wheels (Pinstone 1978), contact with industry representatives suggests that, at least in this country, 1,4-dichlorobenzene is used in vitrified bonding only (Richards 1980). Only one of the three major abrasives manufacturers, Norton Company (Worcester, MA), uses it (Richards 1980). All of the 1,4-dichlorobenzene used for this purpose is assumed to be released to the atmosphere during curing (Richards 1980).

3.3.4.4 Other Uses

The compound 1,4-dichlorobenzene is also used in chemical synthesis, floor waxes and finishes, textiles, and extreme pressure lubricant (Hull 1980). As a reactive intermediate, 1,4-dichlorobenzene can be used to manufacture the dyestuffs 2,5-dichloroaniline and 2,5-dichlorobenzene-sulfonic acid, although a growing market is in the manufacture of polyphenylene sulfide resin, an engineering plastic produced by Phillips Chemical Co. under the trade name Ryton®. The compound 1,2-dichlorobenzene is sold for use in laboratories and was at one time formulated as a heat-transfer medium (Dowtherm E® by Dow Chemical Co.), but that product line has been discontinued (Seifert 1980). Specific data on emissions from the formulation or use of dichlorobenzenes in these applications were not available.

The compound 1,2-dichlorobenzene has also been mentioned in connection with odor control in industrial wastewater plants and sewage treatment plants (Hull 1980). One survey reported that approximately 70 kkg was used in deodorant in sewage plants (Kopp 1980, Hull 1980), but that this did not represent the entire market. Nonetheless, this 70 kkg can serve as a lower limit for estimates of 1,2-dichlorobenzene release to the air from use in odor control (see Table 3-2).

3.4 MUNICIPAL DISPOSAL OF DICHLOROBENZENES

This section deals with the ultimate disposition of dichlorobenzenes discharged to municipal waste facilities. These include publicly-owned treatment works (POTWs) and urban refuse landfills or incinerators.

3.4.1 POTWs

Input of dichlorobenzene to POTWs is largely dependent upon variation in industrial discharges feeding the POTWs and the types of industry in a particular municipal area. A recent EPA study of 20 selected urban POTW facilities with secondary treatment and varying feed conditions produced a materials balance of dichlorobenzenes shown in Table 3-4.

An overall materials balance for municipal disposal, presented in Table 3-5, can be constructed using a total U.S. POTW flow of approximately 10^{11} l/day (EPA 1978d) and simple mean values of 8.3, 1.6, and 2.1 μg/l (influent) and 2, 1.7 and 2 μg/l (effluent) for 1,2-, 1,3- and 1,4-dichlorobenzene, respectively (from Table 3-4). For these calculations influent and effluent flow rates are assumed to be equal (i.e. water loss from sludge removal and evaportion is small compared with influent flows). Using these assumptions, 210 kkg total dichlorobenzes were discharged from POTWs in 1978, while there was an input of 440 kkg (see Table 3-5).

The amount of dichlorobenzene discharged in sludge can be estimated from the dichlorobenzene concentration in sludge and the quantity of dry sludge produced annually, 6.0 x 10^6 kkg (EPA 1979c). Assuming the simple mean 1,2-, 1,3- and 1,4-dichlorobenzene concentrations of POTW wet sludge to be 59, 52 and 105 μg/l, respectively (see Table 3-4), 31 kkg of total dichlorobenzene were released to land as a component of sludge (EPA 1979d).

The amount of dichlorobenzene released to the atmosphere may be approximated by the difference in the above calculations, with the following assumptions: (1) dichlorobenzene recycled within the activated sludge process will eventually be "wasted"; (2) the dichlorobenzene biologically degraded is negligible; and (3) the dichlorobenzene is lost to the atmosphere by mechanical stripping, or aeration (note: volatilization is the primary environmental transport mode for dichlorobenzene). Thus, an estimated 200 kkg of dichlorobenzene are released to the atmosphere from POTWs.

It is of interest to note the presence of 1,3-dichlorobenze in the POTW streams, despite the fact that negligible production of the isomer is reported (Kao and Poffenberger 1979). Possible sources include: contaminant of 1,2- or 1,4-dichlorobenzene-containing products, or analytical errors and artifacts. The former is probably not a significant source, as a contaminant would only be present at ppm levels in the product and not result in wastewater concentrations comparable to the major isomers. The latter theory is a stronger one, due to the similarity of physical properties among all three isomers. Finally, it is important to point out the limited nature of the POTW data, in that 20 plants are taken as representative of the entire U.S. Vastly different totals for influent (110 kkg) effluent (55 kkg), atmospheric emission (55 kkg) and sludge releases (negligible) of dichlorobenzenes result if median values are used in the calculations instead of simple mean values.

Table 3-4 Dichlorobenzene Distribution in POTWs, Sludge; Selected Urban Sites

Plant	Average Flow[a] (10^6 l/day)	Concentration (μg/l)								
		1,2-Dichlorobenzene			1,3-Dichlorobenzene			1,4-Dichlorobenzene		
		Influent	Effluent	Sludge[b]	Influent	Effluent	Sludge[b]	Influent	Effluent	Sludge[b]
1	340	3	1	<10[c]	1	1	<10	3	1	< 10
2	30	4	1	<10	1	3	<10	1	<10	< 10
3	42		ND[d]			ND			ND	
4	320	105	6	282	<5	<5	252	13	2	1,128
5	83	<5	<5	3		ND		<5	<5	15
6	27		ND		3	<1	ND	1	<1	ND
7	190	3	<10	233	<10	<10	35	<10	<10	28
8	87	<2	<2	258	< 2	<2	475	1	<2	325
9	200		ND			ND			ND	
10	87	3	<3	ND	1	< 3	ND	3	<3	ND
11	160	<10	ND	ND		ND			ND	
12	150		ND			ND			ND	
13	64		ND			ND			ND	
14	53		ND			ND			ND	
15	27		ND			ND			ND	
16	550	18	2	ND	< 3	< 3	150	3	< 3	1,217
17	57		ND			ND			ND	
18	240		ND			ND			ND	
19	260	7	5	300	<5	<5	100	2	2	190
20	450	< 5	<5	88		ND			ND	
Median		2.5	1	ND		ND		0.5	0.5	ND
Simple Mean		8.3	2	59	1.6	1.7	52	2.1	2.0	150
Flow Weighted Mean		15	2.8		2.1	2.2		3.0	1.8	

a) The percent industry contribution to flow ranges from <5 to 50%.

b) Combined primary and secondary sludge.

c) For calculation of means and medians, values preceded by < are taken as that number (upper limit) and ND as zero.

d) Not detected.

Source: EPA, 1980c.

Table 3-5 Dichlorobenzene Materials Balance: Municipal POTWs[a] and Refuse (kkg/yr)

Source	Input	Air	Land	Water
POTW	440[b]	200[c]	31[d]	210[b]
Urban				
Incineration	unknown	----------neg[e]----------		
Landfill	520[f]		520[f]	

a) Publicly owned treatment works.

b) Figures calculated from EPA data (see Table 3-4): based on 10^{11} l/day total POTW flow and simple mean values for influent concentrations of; ortho-dichlorobenzene (8.3 μg/l), meta-dichlorobenzene (1.6 μg/l) and para-dichlorobenzene (2.1 μg/l); effluent concentrations of: 2, 1.7 and 2 μg/l, respectively. See Section 3.4.1 for totals calculated from median values.

c) Mathematical difference between input and (Land and Water) values.

d) Based on simple mean values of 59 μg/l (ortho-dichlorobenzene), 52 μg/l (meta-dichlorobenzene) and 150 μg/l (para-dichlorobenzene) for wet sludge loading (see Table 3-4).

e) 99.9% efficiency of incineration; MacDonald *et al.*, 1977.

f) Dichlorobenzene in spent solvent containers and garbage pails (see Table 3-2).

3.4.2 Urban Refuse

Three options for handling of urban refuse are available: energy recovery (primarily by incineration), material recovery, and disposal through incineration or landfills. Urban refuse can be divided into two major components: 1) a combustible fraction (paper, cardboard, plastics, fabrics, etc.); and 2) a noncombustible fraction (ferrous and nonferrous metals, glass, ceramics etc.). There are no data, however, concerning dichlorobenzene emissions from municipal incineration, but these compounds are probably destroyed with over 99.9% efficiency (MacDonald et al. 1977). Dichlorobenzenes could be disposed directly as municipal wastes, in formulated solvent containers or as garbage deodorants. From Table 3-2, this total is 520 kkg (see Table 3-5).

3.5 SUMMARY AND CONCLUSIONS

The chlorobenzenes are produced by direct chlorination of benzene in continuous or batch reactors. The product is a mixture of monochlorobenzene and 1,2- and 1,4-dichlorobenzenes as major products, along with small amounts of higher chlorinated benzenes. In 1978, 27,000 kkg of 1,2- and 33,000 kkg of 1,4-dichlorobenzene were manufactured in the U.S. Total dichlorobenzene exports were 9,500 kkg and imports totalled 640 kkg.

The total amount of dichlorobenzene released to the environment is estimated to be approximately 31,500 kkg, more than one-half of the available U.S. supply. Environmental releases during production totalled 96 kkg to air, 6.3 kkg to land, and 230 kkg to water for 1,2-dichlorobenzene and 240 kkg, 7.7 kkg and 290 kkg for 1,4-dichlorobenzene. These losses occur in vent gases; liquid waste streams from stills, wash tanks and strippers; and sludges. Inadvertent sources of dichlorobenzenes, such as industrial incineration and chlorination of drinking water, do not appear to release significant quantities to the environment.

In general, uses of the dichlorobenzene are responsible for the major losses to the environment. Whereas manufacture accounts for only 2.8% of the environmental releases, use accounts for over 95%. A flow diagram summarizing the dichlorobenzene materials balance is presented in Figure 3-1.

The largest environmental releases are atmospheric, reflecting the volatility of these chlorinated hydrocarbons. Emissions of 1,2-dichlorobenzene (≈ 5,500 kkg) occur primarily during solvent usage [e.g., cleaning or process solvents during toluene diisocyanate (TDI) or 3,4-dichloroaniline production] while the 1,4-isomer (≈ 24,000 kkg) is released as a result of use in mothballs and as a space deodorant. Most of these applications (except TDI process solvent use) represent widespread, dispersive uses, with the potential for exposure to the general public or specific population subgroups as a normal consequence of use.

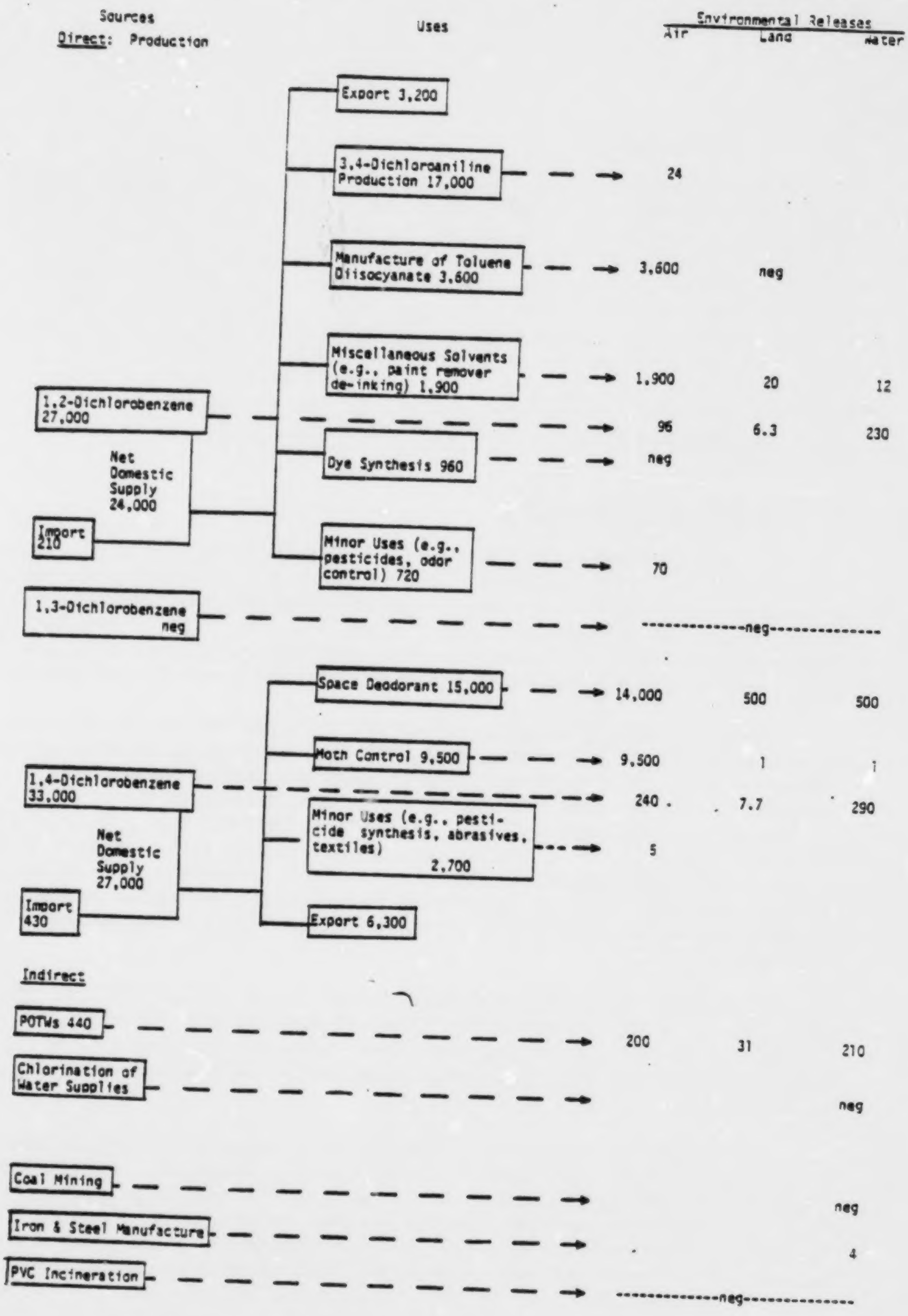

Sources
Direct: Production
Uses
Environmental Releases
Air
Land
Water
Export 3,200
3,4-Dichloroaniline Production 17,000
24
Manufacture of Toluene Diisocyanate 3,600
3,600
neg
Miscellaneous Solvents (e.g., paint remover de-inking) 1,900
1,900
20
12
1,2-Dichlorobenzene 27,000
96
6.3
230
Dye Synthesis 960
neg
Net Domestic Supply 24,000
Import 210
Minor Uses (e.g., pesticides, odor control) 720
70
1,3-Dichlorobenzene neg
neg
Space Deodorant 15,000
14,000
500
500
Moth Control 9,500
9,500
1
1
1,4-Dichlorobenzene 33,000
240
7.7
290
Minor Uses (e.g., pesticide synthesis, abrasives, textiles) 2,700
5
Net Domestic Supply 27,000
Import 430
Export 6,300
Indirect
POTWs 440
200
31
210
Chlorination of Water Supplies
neg
Coal Mining
neg
Iron & Steel Manufacture
4
PVC Incineration
neg

Figure 3-1. Dichlorobenzene Materials Balance Flowsheet, 1978 (kkg/yr)[a]

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[a] Numbers may not add due to rounding to two significant figures.
Inputs not balanced by environmental releases are contained in products (see Table 3-2).

Of the estimated 440 kkg total dichlorobenzenes entering POTWs, calculations indicate that approximately one-half is lost to the air and one-half is discharged to water. The input of dichlorobenzenes to municipal incinerators is uncertain, yet these compounds are probably destroyed with over 99.9% efficiency. Dichlorobenzenes that are dispersed to landfills (520 kkg) arrive there primarily as garbage deodorants or as residue in used solvent containers.

A major goal of this materials balance was to establish a range of uncertainty for the numbers presented. The conclusions are based on a review of all known dichlorobenzene environmental release data. It should be noted, however, that portions of this information are tentative, and, in certain cases, limited to engineering judgement.

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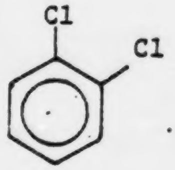
4.0 FATE AND DISTRIBUTION IN THE ENVIRONMENT

4.1 INTRODUCTION

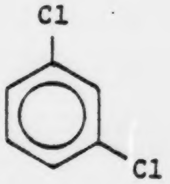
This chapter characterizes the fate processes that determine the ultimate distribution of the dichlorobenzenes in environmental media and, therefore, the opportunities for exposure of humans and other biota. The physiochemical characteristics of dichlorobenzenes are summarized in order to identify the processes that transport or transform the chemical upon its release to the environment (Section 4.2). Modelling efforts undertaken to characterize the fate of dichlorobenzenes in selected environmental scenarios are described (Section 4.3). Monitoring data are presented from STORET and a limited number of surveys that provide indications of concentrations actually detected in environmental media (Section 4.4).

4.2 PHYSIOCHEMICAL CHARACTERISTICS

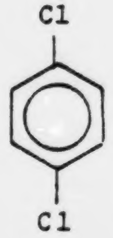
The three dichlorobenzene isomers have the following chemical structures:



1,2-dichlorobenzene
(ortho- or o-dichlorobenzene)



1,3-dichlorobenzene
(meta- or m-dichlorobenzene)



1,4-dichlorobenzene
(para- or p-dichlorobenzene)

The general physical and chemical characteristics relevant to the environmental behavior of these compounds are summarized in Table 4-1. An examination of these data reveals both the similarities and the differences among the three isomers. The three compounds have little variation in such properties as boiling point, density, and vapor pressure. Both 1,2- and 1,3-dichlorobenzene have low melting points (-17.0°C and -24.7°C,

TABLE 4-1. PHYSICAL AND CHEMICAL PROPERTIES OF DICHLOROBENZENES

Property	Dichlorobenzene Isomer			Reference
	1,2-	1,3-	1,4-	
Molecular Formula	$C_6H_4Cl_2$	$C_6H_4Cl_2$	$C_6H_4Cl_2$	
Molecular Weight	147.01	147.01	147.01	CRC Weast (1979)
Melting Point (°C)	-17.0	-24.7	53.1	CRC Weast (1979)
Boiling Point (°C at 1 atm)	180.5	173.0	174.0	CRC Weast (1979)
Density at 20°C	1.3048	1.2884	1.2475	CRC Weast (1979)
Vapor Pressure (mm Hg at 25° C)	1.5	2.28	1.18	Versar (1979)
	1.30	2.20	--	Calc. Chiou, *et.al*. (1977)
Saturated Vapor Conc. (g/m^3 at 25°C)	12	18	9	Calculated: PV=nRT
Water Solubility (mg/ℓ at 25°C)	145	123	79	Verschueren (1977)
	120	--	79	U.S. EPA (1980b)
Partition Coeff.				
Octanol:Water	2500	—	2500	U.S. EPA (1980b)
	2400	2400	2500	Calc.-Chiou, *et al*. (1977)
Sediment:Water	628	--	612	U.S. EPA (1980b)
Fish:Water	209	--	205	U.S. EPA (1980b)
Microbial Degradation Rate Const. ($days^{-1}$)	1.1	--	1.2	U.S. EPA (1980b)
Henry's Law Const. ($atm\ m^3\ mole^{-1}$)	$1.94x10^{-3}$	$2.63x10^{-3}$	$2.72x10^{-3}$	U.S. EPA (1980c)

respectively) and so are liquids at ambient temperatures; 1,4-dichloro benzene, however, is a solid with a melting point of 53.1°C.

Some initial conclusions about the environmental fate of dichlorobenzenes can be made from the physiochemical properties. The fact that the octanol:water and the sediment:water partition coefficients are relatively high tends to indicate that adsorption onto soils and sediments may be a major fate process for dichlorobenzenes discharged into aquatic media. The dichlorobenzenes are only sparingly soluble in water compared with other organic compounds, with saturation concentrations on the order of 100 mg/l (100 ppm). Therefore, neither transport within water (for example, advection), nor transport into the water medium (for example, from rain-out, leaching, or runoff) is expected to be a major environmental fate process. A moderate potential for bioaccumulation is indicated by the fish:water partition coefficient.

The vapor pressures of the dichlorobenzenes are high, corresponding to saturation concentrations in air at 25°C on the order of 0.1-0.2% (v:v); even at 0°C, the dichlorobenzenes have vapor pressures >0.2 mm Hg. The temperature dependence of the vapor pressure is indicated in Figure 4-1. Volatilization is likely to be a major environmental process for dichlorobenzenes in water.

The chemical reactivity of the dichlorobenzenes is expected to be very low under environmental conditions. Although chlorobenzenes can be hydrolyzed under stringent conditions (strong caustic, 300°C) (Morrison and Boyd, 1959), the rate of hydrolysis in ambient water (pH 5-8, T<30°C) will be essentially zero. Likewise, the rate of direct photolysis is expected to be negligible, since the dichlorobenzenes do not absorb UV light in the >290-nm wavelength region characteristic of solar radiation.

The possibility that dichlorobenzenes react with such reactive species as hydroxyl radicals in the atmosphere or RO_2 radicals in aquatic media cannot be ruled out; specific data that would allow estimation of the rate of such reactions have not yet been found. The 1,2- and 1,4-dichlorobenzene isomers were reported by Ware and West (1977) to be quite resistant to autooxidation by the peroxy radical ($RO_2\cdot$) in water; they are also resistant to autooxidation by ozone in the atmosphere. The dichlorobenzenes do, however, react with hydroxyl radicals ($HO\cdot$) in air, with reported half-lives on the order of 3 days (Ware and West 1977).

The rate of biodegradation of dichlorobenzenes in the environment may be sufficiently high to suggest that biodegradation is a major fate process for these chemicals in water. In one set of experiments measuring degradation, a shake-flask culture using acclimated microbial populations showed that within 7 days the 1,2-, 1,3- and 1,4-dichlorobenzenes were 29%, 35% and 16% degraded, respectively. Under the same conditions, benzene was reported to be 100% degraded in the same time period.

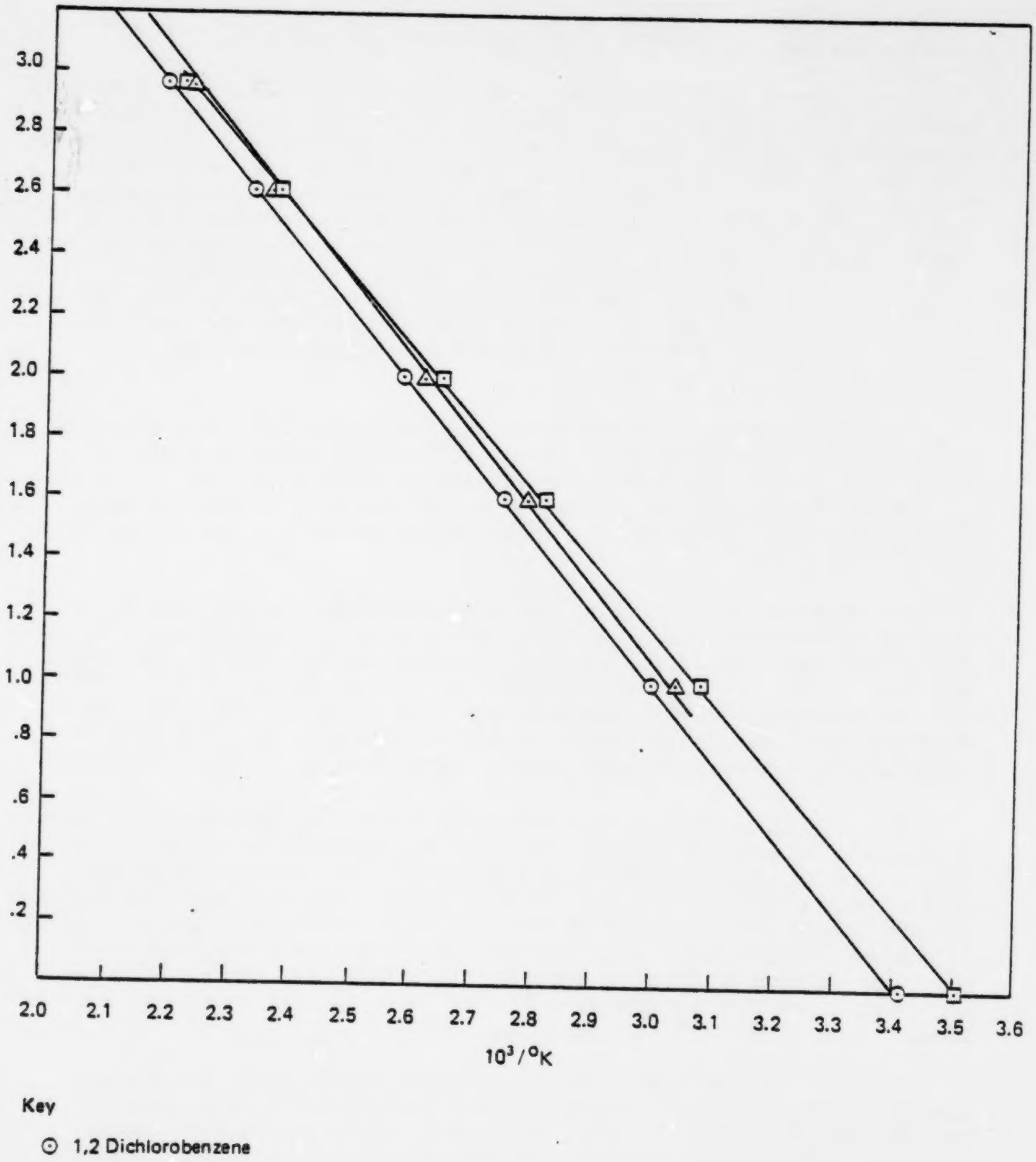


FIGURE 4–1 TEMPERATURE DEPENDENCE OF VAPOR PRESSURE FOR DICHLOROBENZENES

4.3 MODELLING OF ENVIRONMENTAL DISTRIBUTION

4.3.1 Introduction

Several modelling efforts were undertaken to describe important aspects of the behavior of 1,2-dichlorobenzene in selected environmental settings. This isomer was chosen because it is commercially produced and used and because it has the highest water solubility of the three isomers; other properties were quite similar for the three isomers. The Mackay equilibrium model was used to predict the results of physical transport processes on the partitioning of dichlorobenzenes in each environmental compartment when all phases are in equilibrium. The EXAMS (Exposure Analysis Modelling System) developed by the U.S. EPA was used to study the fate of dichlorobenzenes in generalized aquatic environments, and the results were compared with those of the Mackay model. Because volatilization is a major pathway for the dichlorobenzenes in aquatic systems, volatilization half-lives for dichlorobenzene were calculated for a range of wind and current velocities. The results of these modelling efforts are described in this section.

4.3.2 Mackay Equilibrium Partitioning Model

As an initial step in hazard or risk assessments for toxic chemicals, in the planning of laboratory and field tests, and in the interpretation of monitoring data, rough estimates as to the pollutant's environmental distribution can often be made by inspection of the chemical's properties. A simple approach to an initial estimate of environmental partitioning has recently been proposed based upon the fact that in a system at equilibrium, the fugacity of the pollutant must be the same in all phases (Mackay 1979).

In Mackay's Level I approach (the one used here), all environmental compartments (phases) are assumed to be directly or indirectly connected and at equilibrium. The compartments considered are air, surface water, suspended sediments, bottom sediments, sediment biota, and aquatic biota. The Level I calculations require that these compartments be roughly described (volumes, temperature, sediment and biota "concentrations," etc.), and the model output will clearly depend upon the nature of the "environment" selected. Compartment-specific parameters chosen to approximate the EXAMS pond environment are listed in Table 4-2. The Level I calculations do not consider degradation or transport into or out of the selected environment.

A relatively small number of chemical-specific parameters (also listed in Table 4-2) are required to calculate equilibrium partitioning. If one desires an absolute estimate of the equilibrium concentrations in each phase, it is necessary to know the total amount of the chemical that is likely to be in the selected environment. (Note that predicted concentration ratios between two phases will not be affected by the number selected.) Total amount is assumed to be 370 kg (2520 moles) to correspond to the pond accumulation predicted by the EXAMS Model based upon a loading rate

TABLE 4-2. VALUES OF PARAMETERS USED FOR CALCULATING THE EQUILIBRIUM DISTRIBUTION OF 1,2-DICHLOROBENZENE USING THE MACKAY FUGACITY MODEL

CHEMICAL-SPECIFIC PARAMETERS (25°C)

Solubility (mg/l)	145
Henry's Law Constant	1.93×10^{-3}
Adsorption Coefficients:	
suspended sediments	628
sediment	628
biota	209
Total Amount in System	370 kg (2520 moles)

COMPARTMENT-SPECIFIC PARAMETERS (25°C)

Air:	
area	$1 \times 10^4 m^2$
depth	$3 \times 10^3 m$
volume	$3 \times 10^7 m^3$
Water:	
area	$1 \times 10^4 m^2$
depth	2 m
volume	$2 \times 10^4 m^3$
biomass constant	12.9 mg/l
suspended sediment	30 mg/l
Sediment:	
area	$1 \times 10^4 m^2$
depth	$5 \times 10^{-1} m$
volume	$5 \times 10^3 m^3$
biomass content	$50.01 g/m^3$
wet sediment density	$1.85 g/cm^3$
sediment dry weight=	$\frac{100 \times \text{wet weight}}{137}$

of 24 kg/day (see Section 4.3.3). Details of the calculated methods are provided elsewhere (Mackay 1979) and are not repeated here. The results are presented in Table 4-3.

4.3.3 EXAMS Model

The U.S. EPA Athens Environmental Research Laboratory has developed an interactive system designated as EXAMS (Exposure Analysis Modeling System) to carry out exposure analyses for organic chemicals in six freshwater environments (Smith et al. 1977). In performing these analyses, the model assumes "steady-state" behavior and considers the fate and transport of the organic chemical as it passes through a system composed of one or more water and sediment compartments. These compartments have been assembled to represent a simple pond (one water and one sediment compartment), a river (several water/sediment compartments in a row), and a lake (containing "shallow" and "deep" water compartments). Within the aqueous compartments, biota (fish, algae) may be assumed to exist and the extent of bioconcentration of the organic chemical in the species may be calculated.

Using the precompiled environments, plus chemical-specific input parameters, EXAMS models the bulk transport of a chemical (between aqueous compartments) and mixing, as well as the processes of volatilization (loss to the atmosphere), adsorption on sediments and suspended solids (by physical forces or ion exchange), hydrolysis (assumed first-order reaction), photolysis (assumed first-order reaction), biodegradation (with and without light), and dissociation (for organic acids, bases, complexes).

The physical and chemical properties of the three dichlorobenzene isomers do not vary substantially. Therefore, the EXAMS model was run only for 1,2-dichlorobenzene since this isomer is one that is produced in substantial quantities and has the highest water solubility of the three, a characteristic suggesting that it would have the most significant aquatic exposure and effects. Initially, 1,2-dichlorobenzene was modeled in all six of the EXAMS environments (pond, eutrophic lake, oligotrophic lake, river, coastal river, and turbid river). The results showed similar distributions for the three river systems and the three water bodies. On the basis of these preliminary runs, it was decided that modelling of the pond (high biological activity), the oligotrophic lake, and the river would be sufficient to approximate the fate of the dichlorobenzenes in a range of aquatic environments.

The data used as input to the EXAMS model are presented in Table 4-4. Data in the materials balance (Chapter 3.0) indicate that 230 kkg/year of 1,2-dichlorobenzene are released to water during production; releases attributable to individual production plants range from 3.3 kkg/year to 84 kkg/year. Based upon the above data, and with considerations toward ease of model execution, the loading rate for 1,2-dichlorobenzene was set at 24 kg/day (1 kg/hour); compared with the 84 kkg/year discharge, this may be a low estimate. Another source has reported mean industrial dichlorobenzene loadings in the range of 10^{-4} to 13 kg/day (EPA 1980c); based upon these

TABLE 4-3. EQUILIBRIUM PARTITIONING OF 1,2-DICHLOROBENZENE CALCULATED USING MACKAY'S FUGACITY MODEL

Compartment	Partitioning at Equilibrium		
	Moles	Concentration	Percent
Air	881.	4.32 mg/m^3	35.2
Water	7.60	55.9 μg/l	0.30
Suspended Sediment	0.143	35 mg/kg	0.006
Sediment	1610	35 mg/kg dry weight	64.4
Aquatic Biota	0.0206	18 mg/kg	0.0012
Biotic Sediment	0.0200	12 mg/kg	0.0008

TABLE 4-4. INPUT PARAMETERS FOR EXAMS MODELLING OF THE FATE OF 1,2-DICHLOROBENZENE IN GENERALIZED AQUATIC SYSTEMS

Variable	Explanation	Input Value	Reference
MTW	Molecular wt. (g/mole)	147.01	Weast (1979)
KVO	Ratio of volatilization to reareation rate	0.495	SRI (1980)
SOL	Aqueous solubility (mg/l)	145	Verschueren (1977)
KPB	Partition coefficient biomass:water (µg/g)/(mg/l)	209	U.S. EPA (1980b)
HENRY	Henry's Law Constant (atm m^3 $mole^{-1}$)	1.93×10^{-3}	U.S. EPA (1980b)
KOW	Partition coefficient octanol:water	2500	U.S. EPA (1980b)
KBACW1	Second order bacterial degradation rate constant (in water) (ml/cell/hr)	1×10^{-10} 2	SRI (1980)
QTBACW1	Increase in KBACW1 per 10°C change in temperature	2	SRI (1980)
KBACS1	Second order bacterial degradation rate constant (in sediment) (ml/cell/hr)	1×10^{-10}	SRI (1980)
QTBACS1	Increase in KBACS1 per 10°C in temperature	2	SRI (1980)
LOAD	Loading rate (kg/hr)	1	

data the actual exposure concentrations could be up to 100,000 times less than those predicted using a 24 kg/day loading rate.

At chemical concentrations below solubility saturation, maximum concentrations and accumulations will be proportional to loading; self-purification times and percent disposals will be unaffected by changes in loadings. Table 4-5 presents the dichlorobenzene concentrations expected in the three simulated environments at steady-state conditions. Water concentrations in the pond and lake were 3.0 mg/l and 0.15 mg/l, respectively; concentrations in the river systems were much lower largely due to dilution factors. Sediment concentrations were varied; sediment concentrations in the pond system, where there is considerable sediment/water mixing, were almost three orders of magnitude higher than in the other systems.

Table 4-6 gives data on the distribution and transformation of dichlorobenzene in the three environments. The processes for removal from sediment are not very efective. The persistence of 1,2-dichlorobenzene in the pond is much greater than in the lake and river due to the static nature of the pond and to the fact that most of the chemical is residing in the sediment compartment. In the relatively static systems (pond and lake), in which physical transport processses are negligible, volatilization becomes the major removal mechanism, accounting for 91-94.6% of the loss. In the river system, transport downstream is a major removal process, responsible for the lower self-purification time.

A further insight into the impact of a pollutant in aquatic environments is given by examining the persistence of the chemical following termination of the discharge (after the system has reached equilibrium). Table 4-7 outlines the persistence of 1,2-dichlorobenzene following cessation of the 24 kg/day discharge. Within 24 days most of the aqueous 1,2-dichlorobenzene in all three systems will be removed; 99.96% will be removed in one-half day from the water compartment of the river system.

4.3.4 Comparison of Mackay's Equilibrium Model and EXAMS

A pond was picked as the best environment to use in comparing EXAMS results with a Level I Mackay calculation because a pond has the least transport in and out of the environmental system. Comparable EXAMS and Mackay results are summarized in Table 4-8. The total amount of 1,2-dichlorobenzene used in the Mackay model was taken to be equal to the pond accumulation predicted from the EXAMS run with a 24 kg/day loading rate.

In spite of the fact that the assumptions inherent in the two models are different, a comparison of the two sets of data show the results to be in general agreement. The concentrations predicted from the Mackay model are all lower since a large proportion of the 370-kg accumulation from EXAMS has been "removed" by volatilization in the Mackay model. Another major difference between the two models is that the Mackay model is simply a partitioning model, whereas the EXAMS model considers the kinetic data and processes that occur after the chemical has been partitioned

TABLE 4-5. STEADY-STATE CONCENTRATIONS OF 1.2-DICHLOROBENZENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS RESULTING FROM CONTINUOUS DISCHARGE AT A RATE OF 1.0 kg/hour[a]

		Maximum Concentrations						
System	Loading (kg/hr)	Water Dissolved (mg/1)	Water Total (mg/1)	Maximum in Sediment Deposits (mg/kg)	Plankton (μg/g)	Benthos (μg/g)	Total Steady-State Accumulation (kg)	Total Daily Load (kg/day)
Pond	1.0	3.0	3.0	460	630	610	370	24
Oligotrophic Lake	1.0	0.15	0.15	0.73	30	3.3	410	24
River	1.0	0.00099	0.00099	0.024	0.21	0.048	1.2	24

---

[a] All data simulated by EXAMS (U.S. EPA-SERL, Athens, Ga.) model (see text for further information).

TABLE 4-6. THE FATE OF 1,2-DICHLOROBENZENE IN VARIOUS GENERALIZED AQUATIC SYSTEMS[a]

	Percent Distribution		Percent Lost by Various Processes				
System	Residing in Water at Steady-State	Residing in Sediment at Steady-State	Transformed by Chemical Processes	Transformed by Biological Processes	Volatilized	Lost by Other Processes[b]	Time for System Self-Purification[c]
Pond	16.22	83.78	0.0	0.05	91.91	8.05	282.8 days
Oligotrophic Lake	98.11	1.89	0.0	0.0	94.64	5.36	83.78 days
River	75.52	24.48	0.0	0.0	1.44	98.56	18.19 days

---

[a] All data simulated by the EXAMS (U.S. EPA-SERL, Athens, Ga.) model (see text for further information).

[b] Including loss through physical transport beyond system boundaries.

[c] Estimate for removal of ca. 97% of the toxicant accumulated in system. Estimated from the results of the half-lives for the toxicant in bottom sediment and water columns, with overall cleansing time weighted according to the pollutant's initial distribution.

TABLE 4-7. THE PERSISTENCE OF 1,2-DICHLOROBENZENE IN VAROUS GENERALIZED AQUATIC SYSTEMS AFTER CESSATION OF LOADING AT 1 kg/hour)[a]

System	Time Period (days)	% Lost from Water	% Lost from Sediment	% Lost from Total System
Pond	24	87.96	22.28	32.94
Oligotrophic Lake	24	66.74	15.06	65.76
River	0.5	99.96	2.33	76.06

---

[a] All data simulated by the EXAMS (U.S. EPA-SERL, Athens, Ga.) model. See text for further information.

TABLE 4-8. COMPARISON OF RESULTS FROM MACKAY'S EQUILIBRIUM MODEL AND EXAMS FOR 1,2-DICHLOROBENZENE IN A POND SYSTEM

EXAMS Results
(Pond, 24 kg/day loading
370 kg steady state accumulation)

	Maximum Concentrations
Water	3.0 mg/l
Water Biota	630 mg/kg
Sediment Biota	610 mg/kg
Sediment	460 mg/kg

	Accumulation
% in Water	16.22
% in Sediment	83.78

Mackay Results
(370 kg in system)

	Concentrations
Water	0.0559 mg/l
Water Biota	18 mg/kg
Sediment Biota	12 mg/kg
Sediment	35 mg/kg dry weight

	Percent of Chemical per Compartment
% in Water[a]	0.30
% in Sediment	64.4

---

[a] Part of the initial aquatic load has been removed by volatilization.

into a certain compartment. Both models predict that in an equilibrated aquatic ecosystem, most of the 1,2-dichlorobenzene will accumulate in the sediment; however, the Mackay model shows a higher sediment-to-water ratio for the chemical. This apparent discrepancy may be due to the fact that degradation pathways (biolysis, for example) are included in the EXAMS model but are not included in the Mackay model. Once the chemical has been partitioned into sediment in the Mackay model, no allowance is made for degradation and other removal processes. Inclusion of biotransformation processes may also account for the fact that the EXAMS model predicts much higher biotic concentrations for dichlorobenzene.

These data agree well with available monitoring data (presented in Table 4-10). The average ambient water concentration (remarked and unremarked) reported in the STORET Water Quality Information System for 1,2-dichlorobenzene was 29 µg/l; 94% of the unremarked observations were ≤ 100 µg/l. The maximum reported concentration in ambient water was 4660 µg/l.

Volatilization is the primary means of disposition from ponds and lakes and largely controls the persistence of the chemical in these systems. In more dynamic systems, such as rivers, "other" processes (such as advection) are the primary means of disposition. The most significant accumulation is in the sediment, as evidenced by the high maximum concentrations in sediment and by the EXAMS prediction that, within the same period of time, much lower percentages of chemical are lost from the sediment compartment than from the water compartment. Biolysis may be important since the maximum chemical concentrations in both plankton and benthos are high, but this is a relatively minor means of disposition.

4.3.5 Volatilization

The rate of volatilization is dependent upon the chemical properties of the given compound and the physical properties of the water body and the atmosphere above it. For dichlorobenzene, the rate can be determined by a mathematical model using interphase exchange coefficients based on specific chemical and physical properties. The determination of the volatilization rate involves several steps, as shown below.

a) Evaluation of Henry's Law Constant, H, where:

$$H = \frac{P_v}{S}$$

where P_v = vapor pressure at 25°C
S = solubility at 25°C

The values of P_v, S and H for the three dichlorobenzene isomers are shown below.

	1,2-DCB	1,2-DCB	1,4-DCB
P_v (atm)	.002	.003	.002
S (g/1)	.145	.123	.079
H $\left(\frac{\text{atm-m}^3}{\text{mole}}\right)$	.002	.004	.004

b) Compounds with a Henry's Law Constant of less than 3×10^{-7} atm-m^3/mole are often considered non-volatile. The value of this constant for dichlorobenzene indicates that this chemical is highly volatile. Using the dimensional form of the Henry's Law Constant, one can determine the non-dimensional form from which interphase exchange coefficients will be calculated. The non-dimensional Henry's Law Constant, H*, is expressed as:

$$H^* = H/RT$$

Where R = gas constant = 8.2×10^{-5} atm-m^3 /mole-°K

T = temperature = 298°K (equivalent to 25°C)

The values for H* for the three dichlorobenzene isomers are given below:

	1,2-DCB	1,3-DCB	1,4-DCB
H*	8.2×10^{-2}	1.6×10^{-1}	1.6×10^{-1}

c) The liquid phase exchange coefficient, K_ℓ, is based upon the current speed, the depth of the body of water, and the speed of the wind passing over the water surface. As these variables change, the rate of volatilization will also change. For the present example:

V_c = current speed = 1 m/sec

V_w = wind speed = 2 m/sec

D = depth = 1 m

M = molecular weight = 147g

The liquid phase exchange coefficient, k_ℓ, is expressed as (Southworth, 1979);

$$k_\ell = 23.51 \left(\frac{V_c^{0.969}}{D^{0.673}} \right) \sqrt{32/M}\, e^{0.526(V_w-1.9)} = 11.56 \text{ cm/hour}$$

d) The gas exchange coefficient, k_g, can be calculated using the following expression (from Southworth, 1979):

$$k_g = 1137.5\, (V_c + V_n) \sqrt{18/M} = 1194 \text{ cm/hour}$$

e) Employing the liquid and gas phase coefficents and the non-dimensional Henry's Law Constant, the total liquid phase mass transfer coefficient can be expressed as (Southworth, 1979):

$$K_L = \frac{H^* k_g k_\ell}{H^* k_g + K_\ell}$$

For 1,2-dichlorobenzene the value of K_L is 10.34 cm/hour, while for 1,3- and 1,4-dichlorobenzene the value of K_L is 10.90 cm/hour.

f) The volatilization rate constant, k_v, is then:

$$k_v = K_L/100 \text{ cm} = .1034 \text{ hour}^{-1}$$

for 1,2 dichlorobenzene

$$= .1090 \text{ hour}^{-1}$$

for 1,3- and 1,4-dichlorobenzene

g) The half-life of dichlorobenzene in a water body as a function of the volatilization process is:

$$t_{1/2} = (\ln 2)/k_v = 6.4 \text{ hour} - 6.7 \text{ hour}$$

In calculating the liquid phase exchange coefficient, a current speed of 1m/sec and a wind speed of 2m/sec were assumed. The volatilization rate will vary as the wind and current speeds vary. The following are the volatilization half-lives for 1,2-dichlorobenzene as a function of wind and current speed. Note that the variance is small and all half-lives are within an order of magnitude.

VOLATILIZATION HALF-LIVES FOR 1,2-DICHLOROBENZENE

	V_w (m/sec)	
V_c (m/sec)	2	3
1	6.7 hour	4.1 hour
2	3.7 hour	2.3 hour
3	2.5 hour	1.6 hour

4.4 MONITORING DATA

4.4.1 Introduction

Literature reviews and the STORET Water Quality System were the main sources of monitoring data for the dichlorobenzenes under study. The major problems in describing the environmental distribution of these chemicals are the limited amount of literature and sparseness of STORET monitoring data.

The STORET data are discussed first in order to present an overview of the reported national distribution of dichlorobenzenes in the aqueous environment. Subsequent sections of this chapter describe both water and air levels that have been reported in monitoring studies in the published literature.

4.4.2. Overview of Ambient and Effluent Water Concentrations: STORET Data

At least 98% of the effluent concentrations and 94% of the observations recorded for ambient concentrations of dichlorobenzenes are "remarked" values. A remark indicates either that dicholorobenzenes were analyzed for but not detected or that actual values are known to be less than those recorded. Thus, the discussion that follows regarding STORET monitoring data for dichlorobenzene is largely of concentrations not exceeding a reporting (detection) limit rather than the actual concentrations in the environment.

As of September, 1980 both ambient and effluent concentrations of the dichlorobenzenes across the nation were reported to be quite low, with most observations recorded at less than or equal to 10 µg/l. For example, ambient concentrations for the 1,2- isomer indicate that 88% of the 17 unremarked values and 95% of the 349 remarked values are no greater than 10 µg/l. With effluent concentrations for the 1,2-isomer, 58% of the unremarked values and 96% of the 391 remarked values are less than or equal to 10 µg/l. The percentage distribution of unremarked and remarked values for both ambient and effluent concentrations for each isomer is presented in Table 4-9. With so few data and so little definition in the data, an overall trend of higher concentrations near production plants, or other point sources, for instance, could not be discerned.

TABLE 4-9. PERCENTAGE DISTRIBUTION OF AMBIENT AND EFFLUENT CONCENTRATIONS FOR DICHLOROBENZENES IN STORET

	#	Percentage in Remarked Concentration Ranges (μg/ℓ)					#	Percentage in Unremarked Concentration Ranges (μg/ℓ)				
	Obs.	<1	1.1-10	10.1-100	100.1-1000	>1000	Obs.	<1	1.1-10	10.1-100	100.1-1000	>1000
Ambient Data												
1,2-dichlorobenzene	17	12	76	6	0	6	349	29	66	2	3	0
1,3-dichlorobenzene	16	13	81	0	6	0	375	29	69	1	1	0
1,4-dichlorobenzene	24	33	63	0	4	0	390	30	66	1	3	0
Effluent Data												
1,2-dichlorobenzene	7	29	29	14	14	14	391	60	36	3	.5	.5
1,3-dichlorobenzene	6	17	33	17	33	0	394	62	36	2	0	0
1,4-dichlorobenzene	9	33	56	11	0	0	508	70	28	2	0	0

Source: STORET Water Quality Information System, September 1980

Table 4-10 exhibits the unremarked and remarked STORET data for maximum, minimum, and mean concentrations of dichlorobenzenes in ambient waters. Of the 11 major basins with recorded data, the Missouri River basin data reflect the highest maximum concentrations and the highest mean. For the nation as a whole, the mean concentrations for 1,2-, 1,3- and 1,4-dichlorobenzenes from both remarked and unremarked data were calculated as 29 μg/l, 12 μg/l and 14 μg/l, respectively.

Concentrations of dichlorobenzenes in well water samples generally do not exceed 10 μg/l. Monitoring data from 14 water quality stations in the states of Kansas, Washington, Kentucky, Oregon, and South Carolina indicate that the pollutant was analyzed for but not detected, using reporting limits up to 10 μg/l. Where detected, the actual values were reported to be less than the quantification limits.

Table 4-11 displays all STORET data on effluent concentrations in major river basins for each dichlorobenzene isomer, along with a gross analysis. Analysis of this limited data set suggests that maximum effluent levels of 1,2-dichlorobenzene are found in the Northeast (960 μg/l), the Southeast (2500 μg/l), and the Missouri River (316 μg/l) basin. For 1,3-dichlorobenzene, the apparent maximum concentration areas are the North Atlantic (670 μg/l), and the Southeast (2500 μg/l) river basins. The Southeast river basin is also the location of the highest reported level of 1,4-dichlorobenzene. Because the data base is so restricted and since most of the STORET data are remarked, it would be unwise to place much emphasis on the apparent isomer-specific or river basin-specific distribution patterns.

In summary, the STORET effluent data show national mean concentrations centered on 17 μg/l for 1,2-dichlorobenzene, 14 μg/l for 1,3-dichlorobenzene, and 9 μg/l for 1,4-dichlorobenzene. It is somewhat surprising, considering the production and use aspects of the materials balance analysis, that the apparent mean concentrations of all three dichlorobenzene isomers are so similar and that 1,3-dichlorobenzene levels are occasionally higher than those for 1,4-dichorobenzene. This may reflect, in part: experimental uncertainties in isomer designations in analysis and reporting of data; possible differences in reactivities and environmental degradation; or the possibility of some indirect and/or inadvertent sources of the 1,3-dichlorobenzene isomer in the aquatic environment.

4.4.3 Municipal Wastewater

A recent Arthur D. Little, Inc. study (Levins *et al*. 1979) of priority pollutants in municipal wastewater within defined drainage areas found quantifiable levels of dichlorobenzenes in 13% of samples from residential areas, 31% of samples from commercial areas, 57% of [light] industrial area samples, and 56% of POTW influents. The analytical techniques employed in this study gave incomplete resolution of the 3 isomers, and the results have been reported as dichlorobenzenes. The mean concentrations and ranges observed for four U.S. cities were:

TABLE 4-10. AMBIENT CONCENTRATIONS OF DICHLOROBENZENES IN SURFACE WATER: REMARKED AND UNREMARKED DATA IN STORET

Major River Basin	Concentration (µg/1)											
	1,2-Dichlorobenzene				1,3-Dichlorobenzene				1,4-Dichlorobenzene			
	#Obs.	Max.	Min.	Mean[a]	#Obs.	Max.	Min.	Mean[a]	#Obs.	Max.	Min.	Mean[a]
North Atlantic	10	10	10	10	6	10	10	10	10	10	10	10
Southeast	47	20	.00	13	47	20	.00	13	47	20	.00	13
Ohio River	52	100	.02	9	67	20	.01	6	66	20	.01	6
Lake Erie	2	.10	.10	.10					2	20	.20	.2
Upper Mississippi	12	5	2	3	12	5	2	3	12	5	2	3
Lake Michigan	9	1	.00	.33					3	1	1	1
Missouri River	43	4660	2	148	42	400	2	39	44	610	2	58
Lower Mississippi	9	10	.00	3	9	10	.00	3	9	10	.00	3
Western Gulf	15	.00	.00	.00	15	.00	.00	.00	15	.00	.00	.00
Pacific Northwest	86	10	.00	6	86	10	.00	6	86	10	.00	6
Puerto Rico	1	.00	.00	.00	1	.00	.00	.00	1	.00	.00	.00
UNITED STATES	286	4660	.00	29	285	400	.00	12	295	610	.00	14

Source: STORET Water Quality Information System, September 1980.

[a] STORET Mean = average of all data points, remarked as well as unremarked.

TABLE 4-11. CONCENTRATIONS OF DICHLOROBENZENS IN INDUSTRIAL EFFLUENTS: REMARKED AND UNREMARKED DATA IN STORET

Major River Basin	1,2-Dichlorobenzene #Obs.	Max.	Min.	Mean[a]	1,3-Dichlorobenzene #Obs.	Max.	Min.	Mean[a]	1,4-Dichlorobenzene #Obs.	Max.	Min.	Mean[a]
Northeast	101	960	.00	10	101	2	.00	.12	117	57	.10	.75
North Atlantic	71	20	.00	.83	67	670	.00	10	78	20	.00	1
Southeast	52	2500	10	59	52	2500	10	59	62	2500	1	49
Tennessee River	8	10	10	10	8	10	10	10	9	10	1	9
Ohio River	8	100	10	22	8	10	10	10	17	10	1	5
Lake Erie									6	1	1	1
Upper Mississippi	1	4	4	4	1	4	4	4	9	4	1	1
Lake Michigan									1	1	1	1
Missouri River	16	316	1	24	15	5	3	4	26	5	1	3
Lower Mississippi									11	1	1	1
Colorado River									4	1	1	1
Western Gulf	1	.00	.00	.00	1	.00	.00	.00	7	1	.00	.86
Pacific Northwest	32	30	.00	4	32	30	.00	5	39	30	.00	4
California									8	1	1	1
Great Basin									1	.00	.00	.00
Lake Superior									1	1	1	1
Virgin Islands									1	1	1	1
UNITED STATES	290	2500	.00	17	285	2500	.00	14	397	2500	.00	9

Source: STORET Water Quality Information System, September, 1980.

[a] STORET mean is average of all data points, remarked as well as unremarked.

SAMPLE SITE	TOTAL # SAMPLES	% OCCURRENCE OF DCB's	MEAN µg/l	RANGE µg/l
Tap Water	12	0	0	not detected
Residential Areas	47	13	2.8 ± 5.5	0 - 20
Commercial Areas	42	31	7.5 ± 11.3	0 - 26
Industrial Areas	21	57	376	0 - 2187
POTW Influent	18	56	33	0 - 93

The level of industrial activity in each of the four cities studied had a definite effect on the concentrations of dichlorobenzenes. The effluent of one POTW was sampled for comparison with the POTW influent. Dichlorobenzenes were measured in 5 of the 6 influent samples at an average concentration of 25 µg/l; they were not detected in any of the six effluent samples. The detection limit was 10 µg/l.

Earlier work by Kopperman et al.(1975) and by Glaze and Henderson (1975) had reported levels of 1,2- and 1,4-dichlorobenzene in chlorinated wastewater from a Denton, TX facility as 10 µg/l each. An EPA study (Bellar et al.1974) showed an average concentration of 10.6 µg/l of dichlorobenzenes (all isomers) in POTW influents. That work reported levels in POTW effluent of 5.6 µg/l before chlorination and 6.3 µg/l after chlorination. The difference in levels pre- and post-chlorination is probably not significant compared with the uncertainty of the measurement. The data suggest that wastewater chlorination is probably not a major source of dichlorobenzenes in the aquatic environment.

Additional POTW data from a recent EPA study of 20 selected urban POTW facilities with secondary treatment are presented in Chapter 3.0, Table 3-4. The mean and median concentration for the three dichlorobenzene isomers are summarized below:

	Concentration (µg/l)		
	1,2-Dichlorobenzene		
	Influent	Effluent	Sludge
Median	2.5	1	ND
Simple Mean	8.3	2	59
Flow-weighted Mean	15	2.8	
	1,3-Dichlorobenzene		
Median	ND	ND	ND
Simple Mean	1.6	1.7	52
Flow-weighted Mean	2.1	2.2	
	1,4-Dichlorobenzene		
Median	0.5	0.5	ND
Simple Mean	2.1	2.0	150
Flow-weighted Mean	3.0	1.8	

An investigation of chlorinated compounds in the major municipal wastewaters of southern California was conducted by Young et al. (1976). Concentrations of 1,2-dichlorobenzene were recorded from 3.4 µg/l to 34 µg/l (mean 12 µg/l) in the summer months and from 0.42 µg/l to 230 µg/l (mean 50 µg/l) in the fall season. Similarly for 1,4-dichlorobenzene, concentrations in the summer and fall seasons ranged from 1.9 µg/l to 30 µg/l (mean 8 µg/l) and from <0.01 µg/l to 440 µg/l (mean 92 µg/l), respectively.

4.4.4 Drinking Water

The National Organic Monitoring Survey (Symons et al. 1975) found 1,2- and 1,3-dichlorobenzenes in fewer than 5% of the drinking water samples analyzed (Table 4-12). The 1,4-dichlorobenzene isomer was reported more frequently. Mean concentrations for positive results were <2 µg/l, while median concentrations for all samples were <0.005 µg/l for all isomers as indicated in Table 4-12. These data are consistent with the results of an earlier U.S. EPA study (U.S. EPA 1975), which had indicated 1 µg/l, <3 µg/l and 1 µg/l as the highest drinking water concentrations observed for 1,2-, 1,3- and 1,4-dichlorobenzene, respectively. A more recent study (Coleman et al. 1980) reports levels of 9 ng/l and 11 ng/l of 1,2-dichlorobenzene and 10 ng/l and 27 ng/l of 1,4-dichlorobenzene in drinking water samples. Coleman et al. observe that the dichlorobenzenes are reduced to below detectable levels by treatment with granular activated carbon.

4.4.5 Runoff

Young (1976) has reported that a level of 0.05 µg/l of dichlorobenzenes is typical of Los Angeles storm water runoff.

TABLE 4-12. CONCENTRATIONS OF DICHLOROBENZENE DETECTED IN DRINKING WATERS: NATIONAL ORGANIC MONITORING SURVEY, MARCH 1976 THROUGH JANUARY 1977.

Isomer Phase[a]	Number of Positive Analyses per Number of Analyses			Mean Concentration (μg/l) Positive Results Only			Median Concentration (μg/l) All Results[b]		
	I	II	III	I	II	III	I	II	III
1,2-DCB		0/113	4/110			1.5		<0.005	<0.005
1,3-DCB		0/113	2/110			0.10		<0.005	<0.005
1,4-DCB	2/111	20/113	29/110	2.0	0.14	0.07	<1	<0.005	<0.005

Source: Acurex (1981)

[a] Phase I (March-April 1976) Samples shipped and stored at 2° to 8°C for 1 to 2 weeks prior to analyses.

Phase II (May-July 1976) Samples held at 20° to 25°C for 3 to 6 weeks prior to analyses permitting reactions to proceed to end points.

Phase III (November 1976 - January 1977) Samples processed with or without chlorine reducing agent - in these data, samples were processed without quenching additive, so were permitted to react to terminal values.

[b] These are minimum quantifiable limits.

4.4.6 Ambient Surface Waters

Sheldon and Hites (1978) found dichlorobenzene (isomers unspecified) at concentrations of 0.4 µg/l in one out of five winter-time samples of Delaware river water. No detectable levels were found in 11 summer samples from the same source. Jungclaus et al. (1978) detected, but did not quantify, dichlorobenzenes in both the wastewater and the receiving water/sediments near a specialty chemical plant.

Schwarzenback et al. (1979) conducted a 1-year study of 1,4-dichlorobenzene in the central basin of Lake Zurich, Switzerland. The compound is introduced into the lake primarily from domestic sewage effluents. The central basin receives effluent from 12 sewage treatment plants, accounting for approximately 88 kg of 1,4-dichlorobenzene annually; average residence time of water in the basin is 1.2 years. Estimates of 1,4-dichlorobenzene from six vertical concentration profiles taken between November 1977 and November 1978 at the central basin indicated a total quantity of 9 - 13 kg at depths from 0 - 20 m and from 23 - 39 kg between the depths of 20 and 136 m. Experimentation indicated mass transfer to the atmosphere as the predominant elimination mechanism. The average residence time of 1,4-dichlorobenzene in the central basin was calculated at 5 months.

4.4.7 Atmosphere

Concentrations of dichlorobenzenes in ambient air samples collected from various locations across the United States have been reported by Pellizzari (1978). As indicated in Table 4-13, all of the reported observations are <1 µg/m^3; in most instances, the dichlorobenzenes were below detection limits (10-200 ng/m^3 depending on size of air sample) or were reported as "trace" (i.e., presence of chemical detected but at levels too low to quantify). The 1,2- and 1,3- dichlorobenzene isomers were detected most frequently, while 1,4-dichlorobenzene was almost never observed. It should be noted that the data collected by Pellizzari were for the purpose of method development rather than explicitly to monitor dichlorobenzene levels in the environment. The reported concentration levels are very low. Since the purpose of the sampling was not solely to represent ambient concentration levels, sampling techniques may have enhanced identification of the 1,3-dichlorobenzene isomer.

Holzer et al. (1977) reported the identification of 1,3-dichlorobenzene in samples of urban and rural air from Alabama. Quantitative analyses were not reported by Holzer et al. for this chemical but examination of their chromatograms indicates a level of approximately 1µg/m^3 in the urban air and considerably <1 µg/m^3 in the rural air sample.

As part of the same study, Pellizzari examined samples from two industrial locations and a waste disposal site. The air in an area around an American Cyanamid plant in Linden, NJ was found to contain

TABLE 4-13. CONCENTRATION OF DICHLOROBENZENES IN AMBIENT AIR SAMPLES[a]

Sampling Location	Concentration Range (ng/m^3)		
	1,2-DCB	1,3-DCB	1,4-DCB[c]
NJ	<33[b] - 106	<33 - 157	ND
Tulsa, OK	<10 - 100	<10 - 81	ND
Houston, TX	<10 - T[c](175)	<10 - T(175)	ND
Upland, CA	<10 - T(20)	<10 - 382	ND
Magna, UT	<10 - T(77)	<10 - T(77)	<9 - 62
Grand Canyon, AZ	ND	<10 - T(260)	ND
Giesmar, LA	ND	ND	ND
Baton Rouge, LA	ND	ND	ND
Iberville Parish, LA	ND	ND	ND
Pasadena, TX	ND	ND	ND
Deer Park, TX	ND	ND	ND

---

[a] Ranges are for 4-6 observations at each location.

[b] <indicates not detected at level indicated; detection limit varies with sample size.

[c] T = Trace amount detected, level less than the number indicated in parentheses (too low to quantify).

Source: Pellizzari (1978)

2-74 ng/m^3 of 1,2-dichlorobenzene and 1-30 ng/m^3 of another dichlorobenzene isomer. In the area around a DuPont de Nemours plant in Deepwater, NJ, air concentrations of 1,2-dichlorobenzene ranged from trace to 1,300 ng/m^3, while levels of another isomer ranged from trace to 1,200 ng/m^3. Ambient air at the Kin-Buc disposal site at Edison, New Jersey showed levels up to 46,000 ng/m^3 of total dichlorobenzenes (Table 4-14). Again, Pellizzari reports that the 1,2- and 1,3-isomers were most abundant while 1,4- was rarely observed.

Pagnotto and Walkley (1965) report concentrations of 25-35 ppm (150-210 mg/m^3) and 70 ppm (420 mg/m^3) 1,4-dichlorobenzene in workplaces associated with manufacture of that isomer. Levels of dichlorobenzene (isomer not specified) less than 1 ppm were reported at a monochlorobenzene manufacturing plant (SRI 1979).

In a study of dichlorobenzene levels in air in Tokyo, Morita and Ohi (1975) reported 1,4-dichlorobenzene concentrations of 2.7-4.2 µg/m^3 in the central city and 1,5-2.4 µg/m^3 in suburban areas. These levels are 10 to 100 times higher than the data reported by Pellizzari (1978) (Table 4-13) for United States ambient air.

Morita and Ohi (1975) also report some data for indoor air levels of 1,4-dichlorobenzene. Concentrations were 1700 µg/m^3 inside a wardrobe, 315 µg/m^3 inside a closet, and 105 µg/m^3 in a bedroom. These levels suggest that use of 1,4-dichlorobenzene as a moth repellent leads to high concentrations of this chemical within localized areas.

TABLE 4-14. LEVELS OF DICHLOROBENZENES DETECTED IN AIR AT THE KIN-BUC DISPOSAL SITE, EDISON, NJ

Sampling Date	Concentration (ng/m^3)[a,b]		
	1,2-DCB	1,3-DCB	1,4-DCB
6/29/76	<53[c] - 1900	<53 - 34,000	<48 - <81
6/30/76	<40 - 940	<50 - 890	<36 - <65
7/1/76	<49 - 9900	<48 - 3500	<39 - 470
3/24/76-3/26/76	<33 - 12,000	<33 - 27,000	<10 - 7000

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[a] Ranges are for 4-6 observations at each location.

[b] Indicates limit of detection.

[c] <Means not detected at the level indicated; detection limits vary with sample size.

Source: Pellizzari (1978)

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5.0 EFFECTS AND EXPOSURE—HUMANS

5.1 HUMAN TOXICITY

5.1.1 Human and Animal Studies

5.1.1.1 Carcinogenicity

Most available data concerning the carcinogenicity of the dichlorobenzenes are inadequate for valid assessment of risk (IARC 1974) due to small group size, relatively short duration of experimental testing, low exposure levels and/or lack of detail. Girard *et al.* (1969) reported five anecdotal cases of blood disorders in individuals exposed by chronic inhalation and/or dermal contact to 1,2- or 1,4-dichlorobenzene. These included two cases of chronic lymphoid leukemia, two cases of acute myeloblastic leukemia, and one case of myeloproliferative syndrome. However, as with other available data, these reports do not prove a cause-effect relationship, nor do they permit a quantitative risk assessment applicable to the general population. The National Academy of Sciences finds this lack of information "disturbing, in view of the suspected role of p-dichlorobenzene in human leukemia and its apparent ability to undergo metabolic activation and covalent binding to tissue constituents" (NAS 1977).

A study in progress has yielded no evidence of tumor development in $B_6C_3F_1$ mice or Fischer 344 rats (50/sex/species) after 18 months' oral administration of 1,2-dichlorobenzene at 120 mg/kg doses, 5 days/week. However, the treatment has not been completed and histologic examinations have not been performed (L.F. Juodeika, Technical Information Resources Section, Bioassay Program, NCI-NTP, December 3, 1980, personal communication).

5.1.1.2 Adverse Reproductive Effects

No adequate studies are available concerning the embryotoxicity or teratogenicity of the dichlorobenzenes. A potential for transplacental toxicosis or developmental effects may be inferred from human studies that demonstrated the transplacental migration and accumulation in blood of the lower chlorinated benzenes, leading to effects on hormone metabolizing systems. (Dowty and Laseter 1976, Ware and West 1977).

5.1.1.3 Mutagenicity

Data concerning any mutagenic effects of the dichlorobenzenes were inconclusive and limited to submammalian systems. Prasad (1970) reported that treatment of *Aspergillus nidulans* for 1 hour with a 200 μg/ml ether solution of 1,2-, 1,3-, or 1,4-dichlorobenzene resulted in an increase in the number of back mutations. Chlorination in the para-position appeared to have special genetic significance, causing a greater frequency of back mutations.

Anderson *et al*. (1972) found that 1,2-dichlorobenzene was non-mutagenic in an *in vitro* point mutation test system with several strains of histidine-requiring mutants of *Salmonella typhimurium*.

Griffin and Hill (1978) reported no statistically significant increase in the *in vitro* DNA breakage rate of ColE1 plasmid DNA from *Escherichia coli* treated with a 1 mg/ml solution of dichlorobenzene in hexane.

5.1.1.4 Other Toxic Effects

Humans

Most cases of human poisoning from dichlorobenzenes have resulted from long-term inhalation of vapors, although some cases due to ingestion or dermal absorption have been reported. Toxic exposures have been primarily occupational in nature but have also resulted from home use of 1,4-dichlorobenzene or, less frequently, 1,2-dichlorobenzene. In 22 cases of dichlorobenzene poisoning, target systems included the blood or reticuloendothelial system, including bone marrow and/or immune components (17 cases), kidney (1), liver (6), central nervous system (2), respiratory tract (2), and integument (3). General toxic or irritative symptoms were observed in 17 cases, while three cases involved allergy or sensitization (U.S. EPA 1980). Relatively low water solubility and high lipid solubility favor penetration of the dichlorobenzenes by diffusion through most membranes, including pulmonary and gastrointestinal epithelium, brain, hepatic parenchyma, renal tubules and placenta. This allows for wide distribution and accumulation in the tissues leading to possible toxic levels within the body and recirculation of these chemicals for long periods of time (Ware and West 1977).

Three non-occupational cases of poisoning from ingestion of 1,4-dichlorobenzene crystals or pellets have been reported. These include acute poisoning of a 3-year old male (Hallowell 1959), and chronic toxicity to 19-year old (Frank and Cohen 1961) and 21-year-old (Campbell and Davidson 1970) females. The first two instances resulted in hemolytic anemia, while the latter resulted in effects on the central nervous system. All three cases indicated an appreciable absorption of the chemical from the gastrointestinal tract, but no data concerning the quantitative efficiency of the absorption were available.

Several cases of 1,4-dichlorobenzene poisoning have been attributed to inhalation exposure, including one case of pulmonary granulomatosis in a 53-year-old white woman exposed to 1,4-dichlorobenzene crystals for 12-15 years. Macroscopic crystals present in lung lesions were physically similar to those of 1,4-dichlorobenzene (Weller and Crellin 1953). A case of aplastic anemia was reported in a 68-year-old black woman exposed to 5.5-kg 1,4-dichlorobenzene nuggets and 7-kg naphthalene flakes several hours/day for 3 weeks in a room with little air exchange and under extreme heat conditions (Hardin and Baetjer 1978).

Other reports of toxicity attributed to the dichlorobenzenes include six cases of various forms of anemia (Cotter 1953, Petit and Champeix

1948, Perrin 1941, Wallgren 1953), five cases involving severe liver pathology due to chronic inhalation of 1,4-dichlorobenzene vapors, and two cases of anemia due to chronic inhalation of 1,2-dichlorobenzene (Girard et al.1969, Gadrat et al. 1962). The details of these cases were not given, and again, no data on quantitative efficiency of absorption were available.

Hollingsworth et al.(1956) found no organic injury or adverse hematologic effects in workers exposed to average air concentrations of 500 mg/m^3 1,4-dichlorobenzene. A concentration of >960 mg/m^3 was intolerable for an unacclimated person, while 400 mg/m^3 caused painful eye and nose irritation. An odor was detectable at 90-180 mg/m^3 1,4-dichlorobenzene (Hollingsworth et al.1956). In a similar study, occupational exposure to average air concentrations of 90 mg/m^3 1,2-dichlorobenzene caused no organic injury or adverse hematologic effects. Concentrations of 300 mg/m^3 in the air were detectable by the average person, although no eye or nose irritation was experienced (Hollingsworth et al. 1958). Irritation, but no serious effects were noticeable at 600 mg/m^3 1,2-dichlorobenzene (Elkins 1959).

Hollingsworth et al.(1956) reported no notable hazard due to skin irritation or dermal absorption of solid 1,4-dichlorobenzene except under extreme conditions (exact exposures were not specified). In a similar study, liquid 1,2-dichlorobenzene applied to the skin for 15 minutes produced a burning sensation lasting for 1 hour and hyperemia and blisters lasting up to 3 months (Hollingsworth et al. 1958).

A case of allergic purpura was reported in a 69-year old white man 24-48 hours after exposure to 1,4-dichlorobenzene crystals. Serum antibodies for 1,4-dichlorobenzene were still detectable 5 months after the exposure (Nalbandian and Pearce 1965).

A case of contact eczematoid dermatitis was reported in a 47-year old male after chronic skin contact with a solution containing 1,2-dichlorobenzene (Downing 1939).

Experimental Animals

Oral Exposure

Oral LD_{50} (lethal dose to 50% of test animals) values for the dichlorobenzenes are generally in the 500 mg/kg range (RTECS 1978). Acute toxic signs include hyperemia of mucous membranes, increased lacrimation and salivation, excitation followed by sleepiness, ataxia, adynamia, paraparesis, paraplegia, dyspnea, and death attributed to central respiratory paralysis, usually within 3 days. Autopsy showed an enlarged liver with necrosis, submucosal hemorrhage in the stomach and brain edema. At doses of 0.2 LD_{50} per day, 1,2-dichlorobenzene appeared to have cumulative toxic effects causing deaths in one-half of the animals when cumulative doses reached LD_{50} levels. The 1,4- isomer was less toxic than 1,2-dichlorobenzene (Varshavskaya 1967).

Hepatic cirrhosis, focal necrosis and increased liver and kidney weights were noted in rats given 376 mg/kg of either 1,2- or 1,4-dichlorobenzene orally, 5 days/wk for 7 months. The maximum tested dose producing no adverse effects for both isomers was 18.8 mg/kg/day administered by the same schedule (Hollingsworth _et al_. 1956, 1958). Doses of 500 mg/kg/day administered orally to rabbits for 12 months caused central nervous system depression, weight loss, and liver pathology, but no hematologic changes (Hollingsworth _et al_. 1956, Pike 1944). An oral dose of 1000 mg/kg administered to rabbits 5 days/week for several months caused tremors, weakness, nystagmus and reversible eye changes (Pike 1944).

The Russian literature (Varshavskaya 1968) reports toxic effects at doses of 1,2-dichlorobenzene several thousand-fold lower than those reported in other studies. Oral doses to rats of 0.01-0.1 mg/kg/day for several months caused serum and tissue alterations, behavioral abnormalities, and marked reduction in hemoglobin, red-cell, and leukocyte concentrations. A maximum no-detected-effect level of 0.001 mg/kg/day was set; the reason for the discrepancy between this figure and that of 18.8 mg/kg/day as set by Hollingsworth _et al_. (1958) is not clear; exposure levels and their determination were not adequately addressed by Varshavaskaya (1968).

Hepatic porphyria was noted in rats after daily administration by stomach tube of 455-1000 mg/kg 1,2- or 1,4-dichlorobenzene for 5-15 days. An initial marked increase in urinary excretion of urinary coproporphyrin III, increased ALA synthetase (delta-amino-levulinic acid synthetase) activity in the liver, and increased urinary excretion of ALA was observed. In addition, urinary excretion of uroporphyrin and porphobilanogen (PBG) and liver content of protoporphyrin and uroporphyrin all increased.. Clinical observations included anorexia, weight loss, weakness, ataxia, and severe liver damage (Rimington and Zeigler 1963).

Poland _et al._ (1971) reported similar induction of ALA synthetase activity and production of hepatic porphyria in female Sherman rats after daily administration of 900-1000 mg/kg 1,3-dichlorobenzene by gastric intubation for 9 days. However, doses of 800 mg/kg/day administered to rats by intubation for 1, 3 or 5 days produced a biphasic stimulation in the excretion of urinary coproporphyrin III and hepatic ALA synthetase activity (3-4-fold increase), which peaked on days 3 and 1, respectively, and decreased notably by day 5 (although levels were still higher than controls). Data suggest that the decrease in ALA synthetase and urinary coproporphyrin III after 3 days despite continued daily dosage may be the result of an increase in the activity of liver drug-metabolizing systems stimulated by 1,3-dichlorobenzene itself and resulting in decreased serum levels of 1,3-dichlorobenzene. The metabolite 2,4-dichlorophenol did not appear to be the causative agent of the biphasic hepatic porphyria and increased ALA synthetase activity, although these effects can be produced by this metabolite when administered in daily doses of 800-1000 mg/kg. Livers from rats treated with the 800-mg/kg daily doses of 1,3-dichlorobenzene were essentially normal with minimal vacuolization and no evidence of liver damage (Poland _et al_. 1971).

Carlson (1977) found that 1,4-dichlorobenzene at low doses for long periods of time has a low potential for causing hepatic porphyria. Oral administration to female rats of 40, 100 or 200 mg/kg/day 1,4-dichlorobenzene for 30, 60, 90 or 120 days caused only slight increases in liver porphyrins (even after 120 days) and no significant increase in urinary excretion of ALA, PBG or porphyrins. A dose-dependent increase in the liver weight was observed at 30 and 60 days.

Inhalation Exposure

Pike (1944) noted tremors, weakness, nystagmus and reversible eye changes in rabbits exposed via inhalation to 5250 mg/m^3 1,4-dichlorobenzene, 8 hours/day, 5 days/week for 12 weeks. In addition to the above signs, Hollingsworth et al. (1956) reported weight loss, liver degeneration and necrosis in rabbits, rats and guinea pigs exposed to 4,800 mg/m^3 1,4-dichlorobenzene for 7 hours/day, 5 days/week, for 6-7 months. Also, rats exhibited cloudy swelling of renal tubular epithelium, and rabbits showed lung congestion and emphysema. A dose of 950 mg/m^3 over the same time schedule caused growth depression in guinea pigs, increased liver weight in rats and guinea pigs and increased kidney weight, centrolobular cloudy swelling or granular degeneration in rats. A dose of 560 mg/m^3 over this time schedule caused no adverse effects in gross appearance, behavior, growth, organ weights, hematology, urinalysis, gross or microscopic examination of tissues or mortality of rabbits, rats, mice, guinea pigs and monkeys. (Hollingsworth et al. 1956).

Zupko and Edwards (1949) reported the same signs of marked intoxication as described above (Pike 1944) after exposure of 18 male rabbits, 10 male and 10 female rats, and 9 male guinea pigs by inhalation to 100 g/m^3 air of 1,4-dichlorobenzene, 20-30 minutes daily for 30 days. Complete recovery usually ensued within one to several hours; however, some deaths did occur, especially in the guinea pigs (only one of the nine test animals survived beyond 20 exposures). In addition, the majority of animals of all species developed granulocytopenia after repeated exposures. The total leucocytic and erythrocytic counts were not greatly affected. Autopsy of dying or sacrificed animals revealed marked and extensive damage to the kidneys; contrary to other reports, comparatively little damage to the liver was evident. Some damage to the lung tissue was produced, but damage to the heart was negligible (Zupko and Edwards 1949).

Hollingsworth et al. (1958) observed nasal and ocular irritation, drowsiness, coma, massive liver necrosis, and 10% mortality in rats exposed to 4,800 mg/m^3 1,2-dichlorobenzene for 11-50 hours. Rats, guinea pigs, mice, monkeys and rabbits exposed to 560 mg/m^3 1,2-dichlorobenzene 7 hours/day, 5 days/week for 6-7 months showed no adverse effects similar to animals exposed to the same dose of 1,4-dichlorobenzene, as described previously (Hollingsworth et al. 1956).

Cameron and Thomas (1937) found that inhalation of as little as 0.039% 1,2-dichlorobenzene for one-half hour caused liver necrosis in 50% of exposed rats. Exposure of both mice or rats to 0.005% 1,2-dichlorobenzene for 24 hours, of rats to 0.039% for 3-12 hours, or guinea pigs to 0.08% for 24 hours caused liver necrosis in all test animals and some deaths. Maximal changes were usually seen within 24-48 hours, and the extent of the lesions was roughly proportional to the dose. The kidneys showed inconsistent and relatively slight changes confined to the tubular epithelium. Similar studies with 1,4-dichlorobenzene (specific data not given) suggested that the structural position of the chlorine atoms influenced toxicity such that 1,2-dichlorobenzene was more toxic than 1,4-dichlorobenzene (Cameron and Thomas 1937).

Exposure by Injection

Reid et al. (1973) also reported greater hepatotoxicity of 1,2- and 1,3-dichlorobenzene compared with the 1,4- isomer when administered to male Sprague-Dawley rats by intraperitoneal injection at doses of 194, 192 and 500 mg/kg, respectively; minimal necrosis and some glycogen loss was caused by the 1,2- and 1,3-dichlorobenzene, while 1,4-dichlorobenzene caused little to no effect. Injection of the rats with phenobarbital (80 mg/kg) for 3 days prior to these doses of the dichlorobenzenes markedly increased centrolobular hepatotoxicity (glycogen loss with massive or extensive necrosis) caused by the 1,2- and 1,3-dichlorobenzene, but had no effect on the response caused by 1,4-dichlorobenzene (Brodie et al. 1971). In a similar experiment (Reid et al. 1973), intraperitoneal injection of male Sprague-Dawley rats or male C57BL/6 mice with 80 mg/kg phenobarbital for 3 days prior to injection with 73.5 mg/kg ^{14}C-labelled 1,2-dichlorobenzene or 1,4-dichlorobenzene caused increased binding of 1,2-dichlorobenzene in the liver and increased excretion of its urinary metabolites, but had no effect on 1,4-dichlorobenzene metabolism and caused a slight decrease in its binding to centrolobular hepatocytes; the reason for this decrease in binding is not evident (Reid et al. 1973).

The increased hepatotoxicity of the 1,2- and the 1,3-dichlorobenzenes has been attributed to the conversion of the parent compounds by hepatic microsomal enzymes (mixed function oxidases including cytochrome P-450) to active intermediates (epoxides or arene oxides), which product centrolobular necrosis through covalent linkage to the centrolobular hepatocytes. These intermediates are alternatively converted to GSH conjugates, dihydrodiol derivatives, or phenols by enzymes in the soluble fraction of the liver; phenols are excreted, dihydrodiols are converted to catechols, and GSH conjugates are converted to premercapturic acids, which are subsequently excreted (Brodie et al. 1971, Reid et al. 1973).

Copolla et al. (1963) reported an effect on blood coagulation (increase in thromboelastogram reaction and clotting formation times) in guinea pigs injected intramuscularly with daily doses of 125 mg of 1,4-dichlorobenzene for 3 weeks. Totaro (1961) observed weight loss and increased levels of serum transaminases (SGOT and SGPT), with no change in serum aldolase in guinea pigs injected intramuscularly with the same dose of 1,4-dichlorobenzene for 11 or 20 days.

5.1.2 Metabolic Studies

Azouz et al. (1955) detected no 1,4-dichlorobenzene in the feces of rabbits after a single intragastric administration of 500 mg/kg body weight of the compound in oil, a finding suggesting virtually complete absorption under these conditions. Major metabolites, 2,5-dichlorophenol and 2,5-dichloroquinol, were excreted in the urine as glucuronides (36% of the dose) and ethereal sulfates (27% of the dose) with peak excretion on day 2 after administration.

Kimura et al. (1979) found that two sulfur-containing metabolites of 1,4-dichlorobenzene were excreted primarily in the urine of male Wistar rats after a single oral administration (following a 16-hour fast) of 200 mg/kg or 800 mg/kg 1,4-dichlorobenzene. After administration, the level of 1,4-dichlorobenzene was initially higher in the adipose tissue compared with blood or other tissue and within 48 hours, was detectable only in the adipose tissue. The concentration of the metabolite dichlorophenyl methyl sulfoxide (M-1) was greater in the kidney than in the blood, but lower in the liver and adipose tissue. Up to 12 hours, the level of M-2 prevailed, maintaining an appreciable level even after 120 hours (suggesting that M-2 might arise from M-1). The rates of urinary excretion of M-1 and M-2 were very slow (0.031% and 0.122% of dose, respectively, after 96 hours), possibly due to slow release of the parent compound from adipose tissue stores. The rate of urinary excretion of M-2 was initially lower than that of M-1, but increased and prevailed by 48 hours. Urinary excretion of both M-1 and M-2 was much less than that of the major metabolite 2,5-dichlorophenol. Fecal excretion of both M-1 and M-2 was very low.

A single oral dose of 500 mg/kg 1,2-dichlorobenzene administered via stomach tube to rabbits was metabolized primarily to 3,4-dichlorophenol (> 30% of the dose) with minor amounts of 2,3-dichlorophenol (9%), 3,4-dichlorophenylmercapturic acid (5%), and 3,4-(trace) and 4,5-dichlorocatechol (4%). Excretion of 76% of the dose occurred via the urine as conjugates of glucuronide (48%), ethereal sulfate (21%) or mercapturic acid (5%). Peak excretion occurred on day 1 after administration (Azouz et al. 1955). An identical experiment conducted with the 1,4- isomer showed it to be principally metabolized to 2,5-dichlorophenol and, in contrast to 1,2-dichlorobenzene, excreted only as the glucuronide or ethereal sulfate conjugates. Peak excretion occurred on the second day after dosing, possibly reflecting a slower absorption. No 1,4-dichlorobenzene, however, was detected in feces during a 6-day period, indicating essentially complete absorption did occur (Azouz et al. 1955).

Jacobs et al. (1974 a,b) found 1,2-dichlorobenzene accumulated in rat tissue after administration of oral doses of 0.4-2.0 mg/kg/day (length of experiment not stated), indicating significant absorption from the gastrointestinal tract even at low levels of exposure. Tissue accumulation was greater in the fat than in the liver, kidney, heart, or blood (quantitative data not given).

Following administration of a 500 mg/kg dose of 1,3-dichlorobenzene to rabbits via stomach tube, Parke and Williams (1955) reported conversion to the major metabolite 2,4-dichlorophenol (20% of dose) and minor metabolites, 3,5-dichlorophenol, 2,4-dichlorophenyl-mercapturic acid, and 3,5-dichlorocatechol. Urinary excretion of conjugates of the metabolites (accounting for 54% of the dose) peaked on day 1 after administration and included 36% glucuronides, 7% ethereal sulfates and 11% mercapturic acid.

Studies have also indicated absorption of the dichlorobenzenes from the human respiratory tract. Morita and Ohi (1975) reported levels of 2.3 µg/g 1,4-dichlorobenzene in the adipose tissue of 34 subjects (14 male, 20 female) and 9.5 ng/ml 1,4-dichlorobenzene in the blood of six subjects (4 male, 2 female) residing in Tokyo, where ambient air samples contain 2-4 µg/m^3 1,4-dichlorobenzene. A closet treated with this chemical to repel moths contained 315 µg/m^3, while air samples in a bedroom contained 105 µg/m^3. A "wardrobe" was stated to contain 1700 µg/m^3 (Morita and Ohi 1975).

Pagnotto and Walkley (1965) reported rapid respiratory absorption of inhaled 1,4-dichlorobenzene in occupationally exposed persons. Their observation was based upon the rapid urinary excretion of the metabolite, 2,5-dichlorophenol, soon after exposure began. Peak excretion occurred at the end of the work shift. No data on quantitative efficiency of absorption of 1,4-dichlorobenzene were given, although the authors suggest that the level of 2,5-dichlorophenol in the urine at the end of the exposure period correlated fairly well with the average air concentration of 1,4-dichlorobenzene and may, therefore, be useful as an indicator of exposure to the parent compound. Urinary excretion of the other major metabolite of 1,4-dichlorobenzene in man, 2,5-dichloroquinol, was not determined in this study.

5.1.3 Overview

5.1.3.1 Ambient Water Quality Criterion - Human Health

The U.S. Environmental Protection Agency (1980) has established an ambient water quality criterion of 400 µg/l for the protection of human health from the toxic properties of dichlorobenzenes ingested through water and contaminated aquatic organisms. This criterion is based on the maximum chronic no-observed effect level of 13.42 mg/kg/day (18.8 mg x 5/7) reported for rats orally administered either 1,2- or 1,4-dichlorobenzene over a period of 5 to 7 months (Hollingsworth et al. 1956, 1958). Applying an uncertainty factor of 1000, the acceptable daily intake of 1,2- or 1,4-dichlorobenzene for a 70-kg man was calculated to be 0.94 mg/day. The similar toxicities among the dichlorobenzene isomers support the applicability of this value to 1,3-dichlorobenzene as well.

5.1.3.2 Other Health Considerations

Dichlorobenzenes are rapidly absorbed via the lungs and gastrointestinal tract, and can also be absorbed through the skin, with major target systems being the liver, reticuloendothelial system and the central nervous system (see Table 5-1). Liver necrosis has been reported in rats orally administered 376 mg/kg of either 1,2- or 1,4-dichlorobenzene, 5 days per week for 7 months (i.e., 376 mg/kg x 5/7 or 268 mg/kg/day). A no-observed effect level of 13.4 mg/kg/day was established for this species. No chronic toxicity study with a duration greater than 7 months has been completed. A lifetime feeding study with 1,2-dichlorobenzene conducted with both rats and mice is nearing completion. Preliminary data suggest (no histopathology has been done) that ingestion of up to 120 mg/kg 1,2-dichlorobenzene, 5 days per week for 18 months (i.e., 86 mg/kg/day) is not carcinogenic in either species. With the possible exception of this latter study, the inadequacy of available studies on the reproductive effects, carcinogenicity, or teratogenicity have rendered the data insufficient for a valid assessment of risk.

Little specific information is available on human toxicity associated with dichlorobenzene exposure. Anecdotal reports have linked chronic inhalation exposure to various forms of anemia and liver pathology but no quantitative intake data are available. Additional toxicological studies are needed before a reliable estimate of risk can be estimated for humans exposed to the dichlorobenzenes.

5.2 HUMAN EXPOSURE

5.2.1 Introduction

The results of the materials balance analysis (Chapter 3) indicate that 52% of the total U.S. annual production (or 62% of the net domestic supply) of dichlorobenzenes is released into the environment. The potential for exposure of human and non-human populations to these chemicals is, therefore, significant. However, because the dichlorobenzenes are relatively low-volume chemicals and because the sources appear to be widely dispersed, the actual environmental concentrations to which populations may be exposed are generally rather low. The largest releases of the dichlorobenzenes are directly to the atmosphere; furthermore, volatilization is a major fate pathway for dichlorobenzene released to the aquatic environment. Therefore, inhalation is expected to be the primary exposure route for humans.

This section contains a discussion of potential human exposures, based upon the limited amount of monitoring data available. Releases of commercially produced (and used) dichlorobenzenes have been tabulated by state or geographical area when the data were available as an indication of the extent of exposures. Daily exposure levels are estimated for a number of scenarios, using the monitoring data and average intake rates for water and air (ICRP 1975). The data are quite limited, and the resulting exposures are intended to be only approximations of the range of possible exposures to dichlorobenzenes.

TABLE 5-1. ADVERSE EFFECTS OF DICHLOROBENZENES IN MAMMALIAN SPECIES [a]

Adverse Effect	Species	Lowest Reported Effect Level	No Apparent Effect Level
Carcinogenesis	Rat	---	1,2-Dichlorobenzene: Preliminary data suggest 86 mg/kg/day orally for 18 months.
	Mouse	---	
Teratogenesis		No data available.	
Mutagenicity *in vitro*	*Aspergillus nidulans*	200 µg/ml solution of either 1,2-, 1,3- or 1,4-dichlorobenzene.	---
Hepatic necrosis	Rat	268 mg/kg/day orally of either 1,2- or 1,4-dichlorobenzene.	13.4 mg/kg/day orally of either 1,2- or 1,4-dichlorobenzene.
Anemias, liver pathology	Human	Chronic inhalation of 1,2- or 1,4-dichlorobenzene. No quantitative data.	500-600 mg/m^3 occupational exposure to 1,2- or 1,4-dichlorobenzene.
Hemolytic anemia	Human	Ingestion of 1,4-dichlorobenzene crystals. No quantitative data.	---

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[a] Data taken from Section 5.1 of this report.

5.2.2 Waterborne Exposure

5.2.2.1. Geographical Distribution

Monitoring data are too sparse to indicate where humans may be exposed to dichlorobenzene. Tables 5-2 and 5-3 summarize the estimated releases to the aquatic environment of 1,2- and 1,4-dichlorobenzenes, respectively. When available, the geographic distribution of those releases across the United States is also indicated. The tabulated information suggests that exposure might be somewhat lower in the western U.S., but otherwise rather uniform across the country. The available monitoring data (Section 4-4, summarized in Table 5-4,) suggest that patterns of observed concentrations of the dichlorobenzenes detected in aqueous environments do not correspond to the available information concerning the distribution of releases.

5.2.2.2. Exposure through Ingestion

The most direct exposure route for waterborne dichlorobenzenes is ingestion of drinking water. NOMS data for the dichlorobenzenes indicate that the mean non-zero concentrations for 1,2-, 1,3-, and 1,4-dichlorobenzenes were 1.5, 0.1, and 0.07 μg/l, respectively. These data are for Phase III of the NOMS study. The frequency of observation during this phase was 4% for 1,2-dichlorobenzene, 2% for 1,3-dichlorobenzene and 26% for 1,4-dichlorobenezene. Table 5-5 presents the estimated exposure levels for humans consuming 2 liters of drinking water per day. Exposures have been computed using NOMS mean (all non-zero data), median, and maximum concentrations in order to give a range of possible exposure levels.

The potential for exposure to substantial amounts of dichlorobenzenes from drinking water appears to be low. Subpopulations in the vicinity of production or industrial use faciliites might be exposed to transitory, higher levels due to accidental releases, but there are no data to support a quantitative estimate of this type of exposure.

There are no data to indicate that food consumption represents a significant route of human exposure to dichlorobenzenes. However, there are a few observations recorded in the Water Quality Criteria Document (U.S. EPA 1980) that are relevant. Schmidt (1971) reported a disagreeable odor and taste in pork, which could be traced to the use in pig stalls of an odor-control product containing 1,4-dichlorobenzene. Following 3 days of exposure of hens to 20-38 mg/m^3 1,4-dichlorobenzene, eggs were reported to be tainted, although neither hens nor egg production was affected (Langner and Hilliger 1971). There are insufficient data to quantify a human risk due to ingestion of food.

The compound 1,2-dichlorobenzene is registered for use against termites, beetles, bacteria, slime and fungi (Ware and West 1977). The 1,4- isomer is used for control of mildew, tobacco mold, bark beetles and peach tree borers and as a fumigant to control lice, mites, and cockroaches (Ware and West 1977). No uses that would be expected to lead directly to residues in human food chain crops were identified.

TABLE 5-2. VOLUME AND GEOGRAPHIC DISTRIBUTION OF AQUATIC RELEASES OF 1,2-DICHLOROBENZENE[a]

Release Source Type[b]	Location	Estimated Aquatic Release (kkg/year)
1,2-Dichlorobenzene Production % of Production		
36	Delaware	84
22	Michigan	51
14	West Virginia	33
11	New Jersey	26
11	Illinois	26
3	New York	6.6
1	California	3.3
TOTAL		230[c]
Miscellaneous Solvents	Unknown	12
Dye Synthesis; Dye Carrier	9 New Jersey plants; 3 New York, 2 Delaware, 1 Massachusetts, 1 North Carolina, 1 South Carolina, 1 Michigan, 1 Illinois	12
POTWs	Uniform	70[d]

---

[a] Table prepared from data in Section 3.0.

[b] Releases from imported or exported material are unknown and, therefore, not included.

[c] Assuming releases of isomer are proportional to production volumes.

[d] Assuming an even distribution of all three isomers (Table 3-5, footnote b).

TABLE 5-3. VOLUME AND GEOGRAPHIC DISTRIBUTION OF AQUATIC RELEASES OF 1,4-DICHLOROBENZENE[a]

Release Source Type	Location		Estimated Aquatic Release (kkg/year)
1,4-Dichlorobenzene Production[b] % of Production			
45	Delaware		130
18	Michigan		53
18	West Virginia		53
9	New Jersey		26
7	Illinois		21
2	New York		6.8
1	California		3.4
TOTAL			290[d]
Space Deodorant	Northeast	27%	500
	North Central	26%	
	Southeast	17%	
	South Central	17%	
	Southwest	10%	
	Northwest	3.6%	
Moth Control	Northeast	27%	1
	North Central	26%	
	Southeast	17%	
	South Central	17%	
	Southwest	10%	
	Northwest	3.6%	
POTWs	Uniform		70[e]

---

[a] Table prepared from data in Section 3.0, unless indicated otherwise.

[b] Releases from imported or exported material are unknown and therefore not included.

[c] Von Rumker (1974).

[d] Assuming releases of isomer are proportional to production volumes.

[e] Assuming an even distribution of all three isomers (Table 3-5, footnote b).

TABLE 5-4. SUMMARY OF REPORTED AQUEOUS ENVIRONMENTAL CONCENTRATIONS OF DICHLOROBENZENE

Sample	Concentration (μg/1)[a]		
	1,2-DCB	1,3-DCB	1,4-DCB
Drinking Water			
Mean[b] (NOMS)	1.5	0.1	0.07
Median (NOMS)	<.005	<.005	<.005
Maximum[c] (NOMS)	9.1		2.0
Miami, Florida (NORS)	1	0.5	1
Maximum Concentration Reported as of 1975	1	<3	1
Ambient Surface Water			
National Mean[d] (STORET)	29	12	14
Maximum (STORET)	4660	400	610
Effluent Water			
National Mean[d] (STORET)	17	14	9
Maximum (STORET)	2500	2500	2500
Maximum (other)	1100	1100	1100
Municipal Wastewater (Raw)		10-33	
Mean		10-33	
Maximum		376-440	

---

[a] Unless indicated, data are from Section 4.4. of this report.

[b] NOMS Mean is average for all positive data.

[c] U.S. EPA (1978).

[d] STORET mean is average of all data, remarked and unremarked.

TABLE 5-5. ESTIMATED HUMAN EXPOSURE TO DICHLOROBENZENES BY INGESTION OF DRINKING WATER

Sources	Estimated Exposure[a]					
	1,2-DCB		1,3-DCB		1,4-DCB	
	Conc.[b] (μg/1)	Exposure (mg/day)	Conc.[b] (μg/1)	Exposure (mg/day)	Conc.[b] (μg/1)	Exposure (mg/day)
Drinking Water						
-maximum observed	9.1	0.018			2.0	$4x10^{-3}$
-mean observed	1.5	$3x10^{-3}$	0.1	$2x10^{-4}$	0.07	10^{-4}
-median concentration	<.005	$<10^{-5}$	<.005	$<10^{-5}$	<.005	$<10^{-5}$
-water quality criterion[c]	400	0.8	400	0.8	400	0.8

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[a] Estimates of exposure by ingestion are based on drinking water consumption of 2 liters/day.

[b] These concentration data are discussed in Section 4.4 and summerized in Table 5-4.

[c] Total contamination by dichlorobenzene isomers (singly or in total) should not exceed 400 μg/1 (U.S. EPA 1980).

Dichlorobenzenes may occur in plant tissues as products of lindane degradation; dichlorobenzenes, along with other chlorinated benzenes, were identified among a group of lindane metabolites on lettuce and endives (Kohli et al. 1976) and in roots of wheat plants grown from lindane-treated seed (Balba and Saha 1974). Dichlorobenzenes have also been measured in soils as lindane degradation products (Mathur and Saha 1977). The degree of environmental contamination from lindane use is small and, therefore, the degradation of lindane is not expected to be a significant source of dichlorobenzenes in food crops.

5.2.3. Airborne Exposure

5.2.3.1. Geographical Distribution

Tables 5-6 and 5-7 summarize the estimated volume of environmental releases of 1,2- and 1,4-dichlorobenzene, respectively, to the atmospheric environment, with an indication of the geographical distribution of those releases across the United States. (These sources are discussed in detail in Section 3.0.) Table 5-8 summarizes the reported monitoring data on atmospheric environmental concentrations (further discussion of ambient levels may be found in Section 4.4). As shown, the highest concentrations in non-occupational settings result from the dispersive uses of 1,4-dichlorobenzene as deodorizer and as moth repellant. Occupational exposure is expected to be associated primarily with production and with use of 1,2-dichlorobenzene as a chemical intermediate and process solvent.

5.2.3.2. Exposure through Inhalation

Since the largest environmental releases of dichlorobenzene are to the atmosphere, and volatilization is a major removal process for dichlorobenzenes initially released to aquatic media, inhalation is expected to be the major exposure route for humans. Human exposure to atmospheric concentrations of 1,2- and 1,4-dichlorobenzenes has been reviewed for the U.S. EPA Office of Air Quality Planning and Standards (Anderson et al. 1980). The size of the population exposed to various atmospheric concentration levels resulting from point and area source emissions of 1,2- and 1,4-dichlorobenzene was estimated. These data are presented in Table 5-9.

Average respiration rates for an active adult (16 hours) and a sleeping adult (8 hours) are 1.2 m^3/hour and 0.4 m^3/hour, respectively; the average daily rate is about 23 m^3/day (ICRP 1975). Using the data from Table 5-9 and the average respiration rates, exposure levels can be calculated for each concentration level, and populations exposed can be summarized as follows:

TABLE 5-6. VOLUME AND GEOGRAPHIC DISTRIBUTION OF ATMOSPHERIC RELEASES OF 1,2-DICHLOROBENZENE[a]

Release Source Type[b]	Location	Estimated Release (kkg/yr)
Manufacture of Toluene Diisocyanate % of Production		
31	Texas (2 plants)	1110
24	West Virginia (2 Plants)	860
32	Louisiana (3 plants)	1150
9	New Jersey	340
4	Ohio	150
TOTAL		3600
Miscellaneous Solvents	Uniform	1900
Dye Synthesis,Dye Carriers	9 NJ plants; 3 NY; 1 MA; 1 NC; 1 SC; 1 MI; 1 IL	160
1,2-Dichlorobenzene Production % of Production		
36	Delaware	35
22	Michigan	21
14	West Virginia	14
11	New Jersey	11
11	Illinois	11
3	New York	2.7
1	California	1.4
TOTAL		96[c]
Minor Uses	Uniform	70
3,4-Dichloroaniline Synthesis	2 NJ plants; 1 LA plant	24
POTWs	Uniform	67[d]

---

[a] Table prepared from data in Section 3.0 unless indicated otherwise.
[b] Releases from imported or exported material are not included.
[c] Assuming releases of isomers are proportional to its production volumes.
[d] Assuming an even distribution of all three isomers (Table 3-5, footnote b).

TABLE 5-7. VOLUME AND GEOGRAPHIC DISTRIBUTION OF ATMOSPHERIC RELEASES OF 1,4-DICHLOROBENZENE[a]

Release Source Type[b]	Location		Estimated Release (kkg/yr)
Space Deodorant	Northeast	27%[c]	14000
	Northcentral	26%	
	Southeast	17%	
	Southcentral	17%	
	Northwest	3.6%	
	Southwest	10%	
Moth Control			9500
1,4-Dichlorobenzene Production % of Production			
45	Delaware		110
18	Michigan		43
18	West Virginia		43
9	New Jersey		21
7	Illinois		17
2	New York		5.6
1	California		2.8
TOTAL			240[d]
POTWs			67[e]
Minor Uses (pesticide synthesis, abrasives, textiles)			5

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[a] Table prepared from data in Section 3.0, unless indicated otherwise.
[b] Releases from imported or exported material not included.
[c] Von Rumker (1974).
[d] Assuming releases of isomers are proportional to its production volumes.
[e] Assuming an even distribution of all three isomers (Table 3-5, footnote b).

TABLE 5-8. SUMMARY OF REPORTED AIRBORNE CONCENTRATIONS OF DICHLOROBENZENES[a]

Exposure Medium	Concentrations ($\mu g/m^3$)		
	1,2-DCB	1,3-DCB	1,4-DCB
Ambient Air	0 - .106	0 - .382	0 - .062
Air at Waste Disposal Site	0 - 12	0 - 34	0 - 7
Ambient Air at Industrial Location	0 - 1.3	0 - 1.2[b] (1,3 or 1,4-dichlorobenzene)	
1,4-Dichlorobenzene Manufacturing Site			150-420 mg/m^3
Air in Vicinity of Mothball usage:			
bedroom			105
closet			315
wardrobe			1700

---

[a] Data presented in this Table were taken from Section 4.4 of this report, unless indicated otherwise.

[b] Isomers other than 1,2-dichlorobenzene.

TABLE 5-9. ESTIMATED SIZE OF U.S. POPULATION EXPOSED TO POINT AND AREA SOURCE ATMOSPHERIC CONCENTRATIONS OF 1,2- AND 1,4-DICHLOROBENZENE

Concentration ($\mu g/m^3$)	Number of Persons Exposed	
	1,2-Dichlorobenzene	1,4-Dichlorobenzene
100	2	2
50	38	8
25	4,258	30
10	16,315	125
5	26,406	342
2.5	57,100	505,373
1	159,047	9,153,477
0.5	353,618	26,986,006
0.25	1,161,116	61,682,673
0.1	10,105,220	133,639,503
0.05	34,282,399	—

Source: Anderson et al. (1980)

EXPOSURE LEVELS (μg/day)	ESTIMATED SIZE OF POPULATION EXPOSED	
	1,2-DCB	1,4-DCB
< 6 μg/day	47×10^6	195×10^6
11 - 60 μg/day	57×10^4	37×10^6
100 - 2300 μg/day	47×10^3	507

The size of the population with occupational exposure to airborne dichlorobenzenes in the workplace was estimated in a NIOSH survey cited by Hull and Co. (1980). It was estimated, by projection from an industry subsample surveyed, that a total of almost 2 million workers had "full" (>4 hours/week) or "part" (<4 hours/week) exposure to 1,2-dichlorobenzene and that slightly more than one-half million workers had comparable exposure to 1,4-dichlorobenzene. A survey conducted by Hull and Co. for the Synthetic Organic Chemicals Manufacturing Association, based on contacts with all identified shippers and receivers of the chemicals, led to an estimate that many fewer employees (<5000 total) are actually occupationally exposed to the dichlorobenzenes. The Occupational Safety and Health Administration has set standards for dichlorobenzene exposure: 300 mg/m^3 ceiling level, for 15-minute maximum exposure; and 450 mg/m^3 for an 8-hour time-weighted exposure (NIOSH 1979).

Individuals may be exposed to transitory, high levels of 1,4-dichlorobenzene due to consumer use of mothballs. The recommended application rate for that use is approximately 0.16 kg/m^3 (1 lb/100 ft^3) of enclosed space (Von Rumker et al. 1974). Von Rumker states that in order for the moth control agent to be effective the vapors must be kept at such a level in the enclosed space that the vapors would cause eye irritation in humans. Exposure of consumers to such levels would undoubtedly be brief and infrequent because of the unpleasantness of the irritant effect. There is one report (Morita and Ohi 1975) of a dichlorobenzene concentration of 105 μg/m^3 in the general air of a bedroom, associated with mothball usage; the concentration in the closet was 315 μg/m^3 while the vapor concentration of dichlorobenzene inside the wardrobe (where the moth crystals were presumably located) was 1700 μg/m^3 . Confirmation of this concentration as typical of levels arising from use of some mothballs could be significant, since the 105 μg/m^3 concentration is higher than the highest exposure level considered by Anderson et al. (1980) as attributable to point and area ambient air sources. The latter authors did consider mothball use as an area source of 1,4-dichlorobenzene but did not explicitly consider the short-term, local exposures.

Table 5-10 presents the range of estimated inhalation exposures resulting from concentration levels reported in Section 4.4 of this report. The data are very limited and are often reported for a very

TABLE 5-10. ESTIMATED INHALATION EXPOSURES TO DICHLOROBENZENES[a]

Exposure Type (Duration)[b]	1,2-DCB		1,3-DCB		1,4-DCB	
	Concentration ($\mu g/m^3$)	Exposure (mg/day)	Concentration ($\mu g/m^3$)	Exposure (mg/day)	Concentration ($\mu g/m^3$)	Exposure (mg/day)
Ambient Air (24 hrs/day)						
range for 11 locations	0-.106	0 -.002	0-.383	0-.009	0-.062	0-.001
-urban			1	.02	2.7-4.2	.06-.09
-rural			<1	<.02	1.5-2.4	.03-.05
Air Around Industrial Site	.002-1.3		.001-1.2		.001-1.2	
(8 hrs/day		~0-.01mg/8 hr		~0-.01 mg/8 hr		~0-.01 mg/8 hr
(24 hrs/day)		~0-.03		~0-.03		~0-.03
Air at Disposal Site	<.03-12		<.03-34		<.01-7	
(8 hrs/day)		~0-.12 mg/8 hr		~0-.33 mg/8hr		~0-.07 mg/8hr
(24 hrs/day)		~0-.27		~0-.76		~0-.16
Occupational Exposure						
-maximum (8 hrs/day)					4.21×10^5	4042 mg/8 hr
-OSHA 15 minute ceiling (0.25 hrs/day)					2.0×10^5	90 mg/.25hr
-OSHA time weighted average (8 hrs/day)					4.5×10^5	4320 mg/8 hr
Residential Exposure						
-bedroom (10 hrs/day)					105	0.6 mg/10 hr
-closet (0.5 hrs/day)					315	0.2 mg/.5 hr
-wardrobe (0.1 hrs/day)					1700	0.2 mg/.1 hr

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[a] Concentration data are presented in Section 4.4 and Table 5-8.

[b] Estimates of exposure are based on average adult breathing rates of 1.2 m^3/hr for active adult (16 hrs) and 0.4 m^3/hr for a sleeping adult (8 hrs) (ICRP 1975).

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specific environment; therefore, this exposure assessment is not meant to be definitive in terms of the general population. The exposure estimates were computed by multiplying the number of active and sleeping hours by 1.2m^3/hour and 0.4 m^3/hour, respectively, in order to obtain an estimate of the total daily air intake; that intake number was then multiplied by the concentration data to determine exposures. No correction has been made for the amount of dichlorobenzene actually absorbed or metabolized.

5.2.4 Summary

The total volume of releases of dichlorobenzenes to the atmosphere is more than an order of magnitude greater than the releases to the aquatic environment. Furthermore, any dichlorobenzene in aquatic systems would be expected to volatilize rapidly or be partitioned into the sediment. Therefore, the relatively low calculated exposure levels for drinking water are not surprising. The water quality criterion for dichlorobenzenes allows a total daily exposure of 0.8 mg/day, assuming an intake of 2 l/day. Based on the available data, the maximum drinking water exposures were calculated to be 0.018 mg/day 1,2-dichlorobenzene and 0.004 mg/day 1,4-dichlorobenzene. Mean and medium exposure levels range from 10^{-3} to 10^{-5} mg/day.

The exposures due to inhalation of contaminated air are expected to be larger than exposure from ingestion of water. According to Anderson et al. (1980), a very small percentage of the population would be exposed to atmospheric concentrations greater than 2.5 $\mu g/m^3$ from point and area source emissions; the exposure level corresponding to 2.5 $\mu g/m^3$ is estimated to be 0.056 mg/day based on the ICRP (1975) respiration rates. The vast majority of the population is expected to be exposed to dichlorobenzene concentrations less than 0.006 mg/day. Based upon other monitoring data, exposure to dichlorobenzenes in ambient air is generally far less than 0.1 mg/day; the exception is exposure to air at a waste disposal site in New Jersey, where the 24-hour exposure level near the site could be as high as 0.76 mg/day.

The more significant exposures to dichlorobenzene are in indoor environments. One measurement of air in a 1,4-dichlorobenzene plant would give an exposure estimate of 4042 mg/8 hours; the OSHA time-weighted average for an 8-hour period is 4320 mg. Another source of intermittent exposure is indoor air near a source of mothballs. Concentrations measured in a bedroom indicated possible exposure levels of 0.6 mg/10-hour period.

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6.0 EFFECTS AND EXPOSURE--AQUATIC BIOTA

6.1 EFFECTS ON AQUATIC BIOTA

6.1.1 Introduction

This section discusses the levels of dichlorobenzenes that have been determined from laboratory studies to be toxic to marine and freshwater organisms. The data base includes values for all three isomers of dichlorobenzenes, and for representative species from both fresh- and saltwater environments. The available toxicity data are limited to acute effects levels for a few species of fish, invertebrates, and phytoplankton; only one chronic effects value was found.

6.1.2 Fish and Invertebrates

Freshwater toxicity data are presented in Tables 6-1 and 6-2. The acute toxicities reported for 1,3- and 1,4-dichlorobenzenes were similar, whereas 1,2-dichlorobenzene was reported to be more toxic to Daphnia magna by one order of magnitude. The lowest acute effects level was 2,400 μg/l 1,2-dichlorobenzenes for Daphnia magna. The range in freshwater values was from 1,000 μg/l (chronic effects on fathead minnow) to 28,100 μg/l 1,3-dichlorobenzenes for Daphnia. No effects were detected at concentrations below 1,000 μg/l.

Toxicity data for marine organisms are presented in Table 6-3. For all isomers, the most sensitive species was the mysid shrimp, with LC_{50} of 1,199-2,850 μg/l. Dichlorobenzene was acutely toxic to marine fish in the range 7,300-9,660 μg/l. No acute effects on marine organisms have been reported for concentrations below 1000 μg/l.

6.1.3 Other Organisms

The 1,2-dichlorobenzene isomer is apparently used commonly in oyster beds to control oyster drills. It is unclear exactly what exposures affect these organisms, but concentrations as low as 1 mg/l are reported to inhibit the growth of young oysters after 24 hours of exposure. This is approximately equivalent to the acute toxicity level for mysid shrimp. Additional data for marine organisms are presented in Table 6-4.

6.1.4 Plants

Toxicity data for freshwater and marine algae are presented in Tables 6-5 and 6-6. The ranges at which effects to algae were reported are generally higher than the acute toxicity levels for fish and invertebrates: 91,609 - 179,000 ugl for freshwater species, and 44,100-59,100 ug/l for marine phytoplankton.

TABLE 6-1. ACUTE TOXICITY OF DICHLOROBENZENES FOR FRESHWATER FISH AND INVERTEBRATES

Organism	Compound	LC_{50}[a] (μg/1)	Reference
Bluegill (*Lepomis macrochirus*)	1,2-DCB	27,000	Dawson *et al.* (1977)
	1,2-DCB	5,590	U.S. EPA (1978)
	1,3-DCB	5,020	U.S. EPA (1978)
	1,4-DCB	4,280	U.S. EPA (1978)
Cladoceran (*Daphnia magna*)	1,2-DCB	2,440	U.S. EPA (1978)
	1,3-DCB	28,100	U.S. EPA (1978)
	1,4-DCB	11,000	U.S. EPA (1978)
Fathead Minnow (*Pimephales promelas*) (embryo-larval)	1,2-DCB	1,000 (chronic value)	U.S. EPA (1978)

[a] LC_{50} is the concentration lethal to 50% of test organisms.

TABLE 6-2. ACUTE TOXICITY OF DICHLOROBENZENES FOR THE FRESHWATER FATHEAD MINNOW *Pimephales promalas* FOR DIFFERENT EXPOSURE DURATIONS

Compound	LC_{50} (mg/1) at time 24 hr	48 hr	96 hr
1,2-DCB	(77.8-129.9)[a]	76.3	57.0
1,4-DCB	35.4	35.4	33.7

[a] Based upon one partial kill, the best information that the binomial test gives is that authors are 82.7% confident that LC_{50} lies in this interval.

Source: Curtis *et al.* (1978).

TABLE 6-3. ACUTE TOXICITY OF DICHLOROBENZENE FOR MARINE FISH AND INVERTEBRATES

Organism	Compound	LC_{50} (µg/1)	Reference
Tidewater Silverside (*Menidia beryllinia*)	1,2-DCB	7,300	Dawson *et al*. (1977)
	1,2-DCB	9,660	U.S. EPA (1978)
Sheepshead Minnow (*Cyprinodon variegatas*)	1,3-DCB	7,700	U.S. EPA (1978)
	1,4-DCB	7,400	U.S. EPA (1978)
Mysid Shrimp (*Mysidopsis bahia*)	1,2-DCB	1,970	U.S. EPA (1978)
	1,3-DCB	2,850	U.S. EPA (1978)
	1,4-DCB	1,199	U.S. EPA (1978)
Shrimp (*Dalaemonetes pugio*)	1,2-DCB	9,400	Curtis *et al*. (1978)
	1,4-DCB	69,000	Curtis *et al*. (1978)

TABLE 6-4. EFFECTS OF DICHLOROBENZENES ON ANNELIDS AND OTHER MARINE BIOTA

Organism	Compound	Test Duration	Effect	Concentration (µg/l)	Reference
Polychaete worm (*Polydora websteri*)	1,2-DCB	3 hrs	65% emergence from parasitized oysters	100,000	Mackenzie and Shearer (1959)
Polychaete worm (*Nerlis sp.*)	1,2-DCB	3 hrs	70% emergence from parasitized oysters	100,000	Mackenzie and Shearer (1959)
Clam (embryo) (*Mercenaria mercenaria*)	1,2-DCB	48 hrs	LC_{50}	>100,000	Davis and Hindu (1969)
Clam (larva) (*Mercenaria mercenaria*)	1,2-DCB	12 days	LC_{50}	>100,000	Davis and Hindu, (1969)
Polychaete worm (*Polydora websteri*)	1,4-DCB	3 hrs	55% emergence from parasitized oysters	100,000	Mackenzie and Shearer (1959)
Polychaete worm (*Nereis sp.*)	1,4-DCB	3 hrs	100% emergence from parasitized oysters	100,000	Mackenzie and Shearer (1959)

TABLE 6-5. EFFECTS OF DICHLOROBENZENES ON FRESHWATER PLANTS

Organism	Compound	Effect[a]	Concentration (µg/l)
Alga, (*Selenastrum capricornutum*)	1,2-DCB	EC_{50}, 96-hr, chlorophyll *a*	91,600
Alga, (*Selenastrum capricornutum*)	1,2-DCB	EC_{50}, 96-hr, cell number	98,000
Alga, (*Selenastrum capricornutum*)	1,3-DCB	EC_{50}, 96-hr, chlorophyll *a*	179,000
Alga, (*Selenastrum capricornutum*)	1,3-DCB	EC_{50}, 96-hr, cell number	149,000
Alga, (*Selenastrum capricornutum*)	1,4-DCB	EC_{50}, 96-hr, chlorophyll *a*	98,100
Alga, (*Selenastrum capricornutum*)	1,4-DCB	EC_{50}, 96-hr, cell number	96,700

[a] EC_{50}=concentration at which the stated effect was noted.

Source: U.S. EPA (1978)

TABLE 6-6. EFFECTS OF DICHLOROBENZENES ON MARINE PLANTS

Organism	Compound	Effect[a]	Concentration ($\mu g/l$)
Alga, (*Skeletonema costatum*)	1,2-DCB	EC_{50}, 96-hr, chlorophyll *a*	44,200
Alga, (*Skeletonema costatum*)	1,2-DCB	EC_{50}, 96-hr, cell number	44,100
Alga, (*Skeletonema costatum*)	1,3-DCB	EC_{50}, 96-hr, chlorophyll *a*	52,800
Alga, (*Skeletonema costatum*)	1,3-DCB	EC_{50}, 96-hr, cell number	49,600
Alga, (*Skeletonema costatum*)	1,4-DCB	EC_{50}, 96-hr, chlorophyll *a*	54,800
Alga, (*Skeletonema costatum*)	1,4-DCB	EC_{50}, 96-hr cell number	59,100

[a] EC_{50} = concentration at which stated effect is noted.

Source: U.S. EPA (1978)

6.1.5 Conclusions

The concentrations of dichlorobenzenes that have been found to be acutely toxic to marine and freshwater organisms range over two orders of magnitude from approximately 1000 µg/l to 180,000 µg/l. There was some variation among toxicity levels for the same species from different studies; no appreciable difference in toxicity appears to exist between fresh and saltwater organisms. Both *Daphnia magna* and *Daleamonetes pugio* showed an increased sensitivity to the 1,2-dichlorobenzene isomer; however, for most of the other organisms for which there were data, there does not seem to be an appreciable difference in toxicity among the three dichlorobenzene isomers.

6.2 EXPOSURE OF AQUATIC BIOTA

6.2.1 Dichlorobenzene Levels in Aquatic Systems

The only dichlorobenzene isomers that are produced commercially are the 1,2- and 1,4-isomers. Tables 5-2 and 5-3 show that the major environmental releases to aquatic media occur in the Northeast and North Central parts of the U.S. Uses of 1,4-dichlorobenzene as a pesticide which could result in aquatic releases are centered in South Carolina, California, Florida and Maine (Von Runker 1974). Some dichlorobenzene is used for odor control in industrial wastewater treatment plants, and enters water systems throughout the country (Ware and West 1977). Concentration data for POTWs indicated influent levels of 10.6 µg/l; unchlorinated and chlorinated effluent concentrations were 5.6 µg/l and 6.3 µg/l, respectively (Bellar *et al*. 1974).

The STORET (U.S. EPA 1980a) data base for dichlorobenzene is quite limited in that 98% of the data was remarked (observations at or below detection limits). The range of distribution of unremarked (concentrations actually detected) ambient and effluent levels is shown in Table 4-9; there was a total of 79 unremarked observations (57 ambient, 22 effluent) for all three isomers. Only 7 observations were greater than 100 µg/l. The STORET data do not reflect the fact that discharge due to industrial activity is expected to be higher in the Northeast and North Central areas.

The threshold for the lowest (chronic) toxic effects to aquatic organisms exposed to dichlorobenzenes was about 1000 µg/l. The 1,2-dichlorobenzene isomer was actually observed once in ambient waters at a concentration above 1000 µg/l, i.e., at 4660 µg/l in the Missouri River; one unremarked effluent observation of that isomer above 1000 µg/l was also made. Table 6-7 gives a summary of the remarked and unremarked STORET data.

TABLE 6-7. SUMMARY OF STORET DATA (Remarked and Unremarked)

	Compound	Maximum Concentration (μg/1)	Mean Concentration (μg/1)	% Unremarked Data ≤10 μg/1	% Remarked Data ≤10 μg/1
Ambient Water	1,2-DCB	4660	29	88	95
	1,3-DCB	400	12	94	98
	1,4-DCB	610	14	96	96
Effluent	1,2-DCB	2500	17	58	96
	1,3-DCB	2500	14	50	88
	1,4-DCB	2500	9	89	98

The solubility of dichlorobenzene is low (145, 123 and 79 mg/l for the 1,2, 1-3, and 1-4 isomers, respectively) and the sediment-water partition coefficient is moderately high. These factors, in addition to relatively high volatility, indicate that these compounds would not remain in the water column, but rather adsorb to soils and sediments or volatilize to the air. EXAMS (U.S. EPA 1980b) modelling data for 1,2-dichlorobenzene bear out these observations. Based on a loading rate of 1.0 kg/hour, which approximates the environmental release data presented in Chapter 3.0, 75% of the 1,2-dichlorobenzene discharged to the river (the system most likely to receive industrial, aquatic releases) would be dissolved in water at equilibrium, with a steady state concentration of 0.99 µg/l; 24% would be residing in the sediment. The EXAMS data also show that the persistence of 1,2-dichlorobenzene in the river system following cessation of the discharge would be low. Within 12 hours, 99.9% would be removed from the water column, 23% would be removed from the sediment, and only 24% of the compound would be remaining in the total system. For the pond and oligotrophic lake, EXAMS data indicate that volatilization and transport to the sediment are the major processes for removal from the water column. However, the steady-state accumulation and the persistence in these more static systems are much greater than in the river system.

The above discussion suggests that any dichlorobenzene that is released to aquatic media and dissolved in the water column could be expected to be diluted, volatilized, or adsorbed into sediment. Availability to the aquatic biota would not be very high.

It appears that low level discharges will ordinarily not persist near the source, particularly in a river, where transport downstream is quite important. There have, however, been three reported fish-kills caused by dichlorobenzene. The available data from these incidents are summarized in Table 6-8, below. In all three cases the exact concentration of dichlorobenzenes was unknown, but an accidental spill of large quantities of the compound resulted in the fishkill. Dilution did prove to be important in all three incidents, as in no case did serious effects last longer than one day.

6.2.2 Conclusions

Based on the limited monitoring data, it appears that the dichlorobenzenes are found in ambient and effluent water at concentrations predominantly in the low ppb range (10 µg/l or less). Important environmental fate processes in turbid systems include dilution and physical transport downstream and, to a lesser extent, volatilization; volatilization and transport to the sediment are the predominant processes in more static systems. There is no evidence to indicate, however, that these compounds will persist in the sediments to any great degree; the EXAMS data show that 15-22% of the DCB in the sediment (pond and lake) will be removed within 24 days after the discharge is stopped. Any higher concentrations that occur as a result of accidental spills, direct discharge to streams, or off-site migration of dichlorobenzene from a (land) disposal site would be expected to be diluted or dissipated fairly quickly and not result in persistent or long-term exposure.

TABLE 6-8. SUMMARY - REPORTED FISH KILLS DUE TO DICHLOROBENZENE^a- 1970 - 1980.

Date	Location	Stream	Fish Killed	Extent and Duration of Effects	Source
May 1973	Tennessee	Beaver Creek	536 (20% game species)	4.4 mi.stream for one day	chemical plant
April 1975	Parkersburg West Va.	Worthington Creek	41,945 (99% non-game)	one-mile of river for one day	DCB from nearby chemical dump flushed down storm drain
May 1979	Sevier City, Tenn.	Dudley Creek	360 minnows and rainbow trout	2 miles stream for one day	DCB use in washing city equipment

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[a] All data from EPA Monitoring and Data Support Division Files, 1980.

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7.0 RISK CONSIDERATIONS

7.1 INTRODUCTION

The purpose of this chapter is to evaluate the risks to humans and aquatic biota resulting from exposure to dichlorobenzenes in the environment. A quantitative analysis of risk is hampered by the limited data base for predicting the health effects and levels associated with those effects, as well as by the scarcity of monitoring data available to use in assessing the extent of exposure to the dichlorobenzenes.

7.2 HUMANS

7.2.1 Statement of Risk

The full extent of risk to humans resulting from environmental exposure to dichlorobenzene cannot be assessed quantitatively at present, due to the limited availability of adequate toxicological data. Dose levels at which acute effects upon humans or mammals have been observed are generally far above the estimated human exposures via inhalation or ingestion. However, the potential chronic effects of dichlorobenzenes are still uncertain. Although dichlorobenzenes are considered by EPA's Carcinogen Assessment Group to be of potential concern with regard to carcinogenicity, preliminary data from lifetime feeding studies with 1,2-dichlorobenzene for rates and mice exposed to 120 mg/kg, 5 days/week (i.e., 86 mg/kg/day) suggest no carcinogenic activity. Decisions regarding the oncogenic capability of 1,2-dichlorobenzene, however, should be deferred pending completion of the study. The available information about mutagenic, teratogenic, and other toxicological effects is also not sufficient to permit a quantification of risk to humans at this time. Consequently, the risk associated with exposure to the dichlorobenzenes must be evaluated qualitatively, through a comparison of estimated exposure levels with the available data concerning observed effect levels.

Subchronic studies indicate that ingestion of 13.42 mg/kg/day is a no-observed-effect level for rats. In setting the current water quality criterion, the EPA applied a safety factor of 1000 to this level; extrapolation of this value to humans results in an estimated acceptable daily intake of 0.94 mg/day for a 70-kg man. Humans rarely appear to be exposed to concentrations of the dichlorobenzenes in environmental media that are high enough to cause apparent adverse effects. Exposure for the general population from ambient air and drinking water is usually in the range of 0.001-0.09 mg/day. Exposure from industrial contamination of ambient air or residential use of dichlorobenzene moth repellants is expected to be less than 1 mg/day; these levels correspond to specific subpopulations. Each of the environmental exposure scenarios reviewed results in an exposure level at, or below, the daily intake allowed by the current EPA water quality criterion for the protection of human health. Thus, existing health effects data, coupled with estimated levels of exposure suggest that the risk associated with exposure to dichlorobenzenes in the environment is not unreasonable. However, much uncertainty exists with respect to exposure and long-term health effects, and subsequent findings could alter these conclusions.

7.2.2 Discussion

The dichlorobenzenes have been shown to be absorbed by humans, as well as laboratory animals, via the lungs and gastrointestinal tract; absorption through the skin has also been shown. The major target systems are the liver, reticuloendothelial system and the central nervous system. The inadequacy of available studies on the reproductive effects, carcinogenicity, or teratogenicity have rendered the data insufficient for a valid assessment of these risks. The 1,4-dichlorobenzene isomer has been linked anecdotally with a few cases of human leukemia, but a cause and effect relationship could not be reliably inferred from these reports. Preliminary data from lifetime feeding studies with rats and mice given 1,2-dichlorobenzene suggest no induction of oncogenic effects.

The doses that have been associated with adverse effects of the dichlorobenzenes are summarized in Table 7-1. No serious effects were noticed in humans following inhalation exposure to 600 mg/m^3 1,2-dichlorobenzene; no organic injury or adverse hematologic effects were found in workers exposed to 500 mg/m^3 1,4-dichlorobenzene. As discussed in Section 5.1, no-effects levels of 13.4 mg/kg/day were observed for rats ingesting either 1,2- or 1,4-dichlorobenzene for 7 months. It should also be noted that a Russian study indicated a much lower no-effects level of 1 μg/kg/day for 1,2-dichlorobenzene; however, these data are difficult to evaluate because exposure levels and their determination were not adequately addressed in the published report of this work. Very few data are available on the effects of 1,3-dichlorobenzene. However, one study reported that a dose of 192 mg/kg 1,3-dichlorobenzene was found to be hepatotoxic in rats when injected interperitoneally; 500 mg/kg 1,4-dichlorobenzene caused little or no effect.

The dichlorobenzene exposure levels have been estimated for various concentrations in atmospheric and aquatic media by assuming specific intake rates of air and water for a 70-kg person; these are discussed in Section 5.2 and are summarized in Table 7-2. It should be mentioned that these estimates are based on a number of assumptions, and that there is considerable uncertainty involved. In addition, the size of subpopulations exposed to elevated atmospheric concentrations of dichlorobenzenes from industrial activities or mothball use, as well as numbers of people exposed to any contamination in drinking waters not yet monitored, is unknown.

It is evident that exposure to indoor air concentrations (occupational environments and air in vicinity of mothball use) is potentially much higher than exposure to ambient concentrations of dichlorobenzenes. Based on a duration of exposure of 10 hours, a person could be exposed to 0.6 mg/day dichlorobenzene in a room in close proximity to wardrobe storage of mothballs: breathing the air inside the wardrobe could increase the exposure by

TABLE 7-1. REPORTED DOSES ASSOCIATED WITH EFFECTS OF DICHLOROBENZENES IN MAMMALS

Route/Effect	Level			
	1,2-DCB	Ref[a]	1,4-DCB	Ref[a]
Inhalation				
Odor Threshold	300 mg/m^3	Hollingsworth *et al*.1958	90-180 mg/m^3	Hollingsworth *et al*.1956
Irritation-human	600 mg/m^3	Elkins 1959	400 mg/m^3	Hollingsworth *et al*.1956
No organic injury or adverse hematologic effects-human	90 mg/m^3	Hollingsworth *et al*.1958	500 mg/m^3	Hollingsworth *et al*.1956
No serious effects-human	600 mg/m^3	Elkins 1959		
LCLo - rat	5000 mg/m^3 for 7 hr	Pike 1944		
Ingestion				
Oral LDLo - human	500 mg/kg	RTECS 1978	500 mg/kg	RTECS 1978
Oral LD_{50} - rat	500 mg/kg	RTECS 1978	500 mg/kg	RTECS 1978
No adverse effects - rat	13.4 mg/kg/day	Hollingsworth *et al*.1956	13.4 mg/kg/day	Hollingsworth *et al*.1956
Odor threshold	2 µg/l	Varshavskaya 1967	2 µg/l	Varshavskaya 1967
Taste threshold	0.1 µg/l	Varshavskaya 1967	6 µg/l	Varshavskaya 1967

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[a] References are given in Chapter 5.0.

TABLE 7-2. SUMMARY OF U.S. SUBPOPULATIONS EXPOSED TO VARIOUS LEVELS OF DICHLOROBENZENES

Exposure Route	Estimated Exposure Levels		Population Description
	1,2-Dichlorobenzene	1,4-Dichlorobenzene	
Ingestion of drinking water	avg. 2.8 μg/day[a] max. 18 μg/day	avg. 0.14 μg/day[a] max. 4 μg/day	4-26% of general population[a] certain municipalities
Inhalation			
ambient air	≤ 2 μg/day	≤ 90 μg/day	general population
air near sources	10-270 μg/day	10-160 μg/day	about 0.2% of population
indoor air		~ 1000 μg/day in worst case	users of mothballs
occupational environment		<4 g/day (8 hr)	1,4-dichlorobenzene manufacturing plant

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[a] The National Organic Monitoring Survey (NOMS; Table 4-12) reported that 1,2-dichlorobenzene was detected in 4 of 110 samples taken from a cross section of public water supplies; 1,4-dichlorobenzene was found in 29 of 110 samples in the same study.

0.2 mg/6 minutes. An additional source of local, high environmental concentrations of dichlorobenzene may be associated with the 100% 1,4-dichlorobenzene blocks used for odor control in toilet bowls, urinals, garbage pails and diaper pails. However, there are no data with which to quantify a risk estimate for this exposure route.

From the data in Section 5.2, it is apparent that a significant exposure to dichlorobenzenes exists in the workplace. A maximum concentration of 421 mg/m^3 1,4-dichlorobenzene was measured in a manufacturing plant; this level would result in a daily exposure of 4.0 g/day assuming an 8-hour duration of exposure. This level of exposure is within the range of exposures where acute health effects have been observed (see Figure 7-1). Eye and/or nose irritation, but no organic injury or adverse hematologic effects, was observed in workers exposed to average air concentrations of 500 mg/m^3 1,4-dichlorobenzene (Hollingsworth et al. 1956) or 600 mg/m^3 1,2-dichlorobenzene (Elkins 1959). The OSHA has set an 8-hour time-weighted average of 450 mg/m^3 for dichlorobenzenes. Further discussion of the risk from occupational exposure is beyond the scope of this risk assessment. The impact of industrial activity, however, is relevant in that the ambient air concentrations near plants and disposal sites where dichlorobenzenes are present are one to two orders of magnitude higher than non-industrial areas.

The exposure levels estimated from actual dichlorobenzene concentration data can be compared with the available health effects data to determine the apparent margin of safety associated with each exposure scenario. These comparisons are presented in Tables 7-3 and 7-4 for 1,2- and 1,4-dichlorobenzene, respectively; there are insufficient data to make the comparison for 1,3-dichlorobenzene. As a worst case estimate, exposure from ingestion of 2 liters/day of ambient water has also been included.

For the general population, the probability of acute health effects to humans subjected to various exposure levels is shown graphically in Figure 7-1. The probability of exposure to different amounts of dichlorobenzenes (mg/day) has also been plotted for the ingestion and inhalation exposure routes. It appears that inhalation is the more significant route of exposure for most of the U.S. population. Drinking water accounts for relatively low exposures, although heavily contaminated drinking water in some local areas could possibly result in higher exposure levels.

The curves in Figure 7-1 represent approximate exposure and effect levels for both 1,2- and 1,4-dichlorobenzene. In reality, these levels are slightly different for the two substances, but the diagram sufficiently illustrates the orders-of-magnitude gap between environmental exposures and the levels at which effects may occur. The existing criteria and standards for these substances are listed in Table 7-5. It is clear from the diagram that the ambient water quality standard provides adequate protection against acute risks to humans via the aquatic environment. The results of ongoing and/or future studies of chronic effects of the dichlorobenzenes could lead to significant revisions in criteria/standards and thus require a reassessment of risk.

TABLE 7-3. MARGINS OF SAFETY FOR 1,2-DICHLOROBENZENE EXPOSURE SCENARIOS

Scenario	Typical Exposure (mg/day)	Lowest Reported Effects Level (mg/day)	Estimated Margin of Safety[a]
Ingestion of Drinking Water			
- Average	0.003	> 938[b]	$> 3.1 \times 10^5$
- Maximum	0.018	> 938[b]	$> 1.9 \times 10^4$
Ingestion of Ambient Water			
- Average	0.058	> 938[b]	$> 1.6 \times 10^4$
- Maximum	9.3	> 938[b]	$> 1 \times 10^2$
Inhalation			
- Ambient Air	<.002	13,800[c]	$> 6.9 \times 10^6$
- Air near industrial site	<.03	13,800[c]	$> 4.6 \times 10^5$
- Air near disposal site	<.27	13,800[c]	$> 5.1 \times 10^4$

[a] Margin of Safety = lowest reported effects level ÷ estimated exposure level.

[b] No adverse effects (rat) reported at 13.4 mg/kg/day x 70-kg/person = 938 mg/day.

[c] Irritation in humans reported at 600 mg/m^3. Assuming 23 m^3/day, gives level of 13.8 g/day. No serious effects were reported at this dose.

TABLE 7-4. MARGINS OF SAFETY FOR 1,4-DICHLOROBENZENE EXPOSURE SCENARIOS

Scenario	Typical Exposure (mg/day)	Lowest Reported Effects Level (mg/day)	Estimated Margin of Safety[a]
Ingestion of Drinking Water			
- Average	0.0001	> 938[b]	$> 9.4 \times 10^6$
- Maximum	0.004	> 938[b]	$> 2.3 \times 10^5$
Ingestion of Ambient Water			
- Average	0.028	> 938[b]	$> 3.3 \times 10^4$
- Maximum	1.22	> 938[b]	$> 7.7 \times 10^2$
Inhalation			
- Ambient air	<.001	9200[c]	$> 9.2 \times 10^6$
- Rural air	<.05	9200[c]	$> 1.8 \times 10^5$
- Urban air	<.09	9200[c]	$> 1.0 \times 10^5$
- Air near industrial site	<.03	9200[c]	$> 3.1 \times 10^5$
- Air near disposal site	<.16	9200[c]	$> 5.7 \times 10^4$
- Air in occupational environment (max.)	4042 mg/8 hr	9200[c]	2.02[d]
- Air in bedroom	0.6 mg/10 hr	9200[c]	1.5×10^4
- Air in closet	0.2 mg/0.5 hr	9200[c]	4.6×10^4
- Air in wardrobe	0.2 mg/0.1 hr	9200[c]	4.6×10^4

[a] Margin of Safety = lowest reported effects level ÷ estimated exposure level.

[b] No adverse effects (rat): 13.4 mg/kg/day x 70 kg/person = 938 mg/day.

[c] Irritation in humans reported at 400 mg/m^3 (9200 mg/day); no adverse hematologic effects at 500 mg/m^3.

[d] The margin of safety shown is in reference to the lowest reported effects level. The acceptable daily intake allowed by the OSHA standard is 4320 mg/day (450 mg/m^3 x 1.2 m^3/hr x 8 hr). The associated margin of safety for the maximum calculated exposure with respect to the OSHA standard is 1.1.

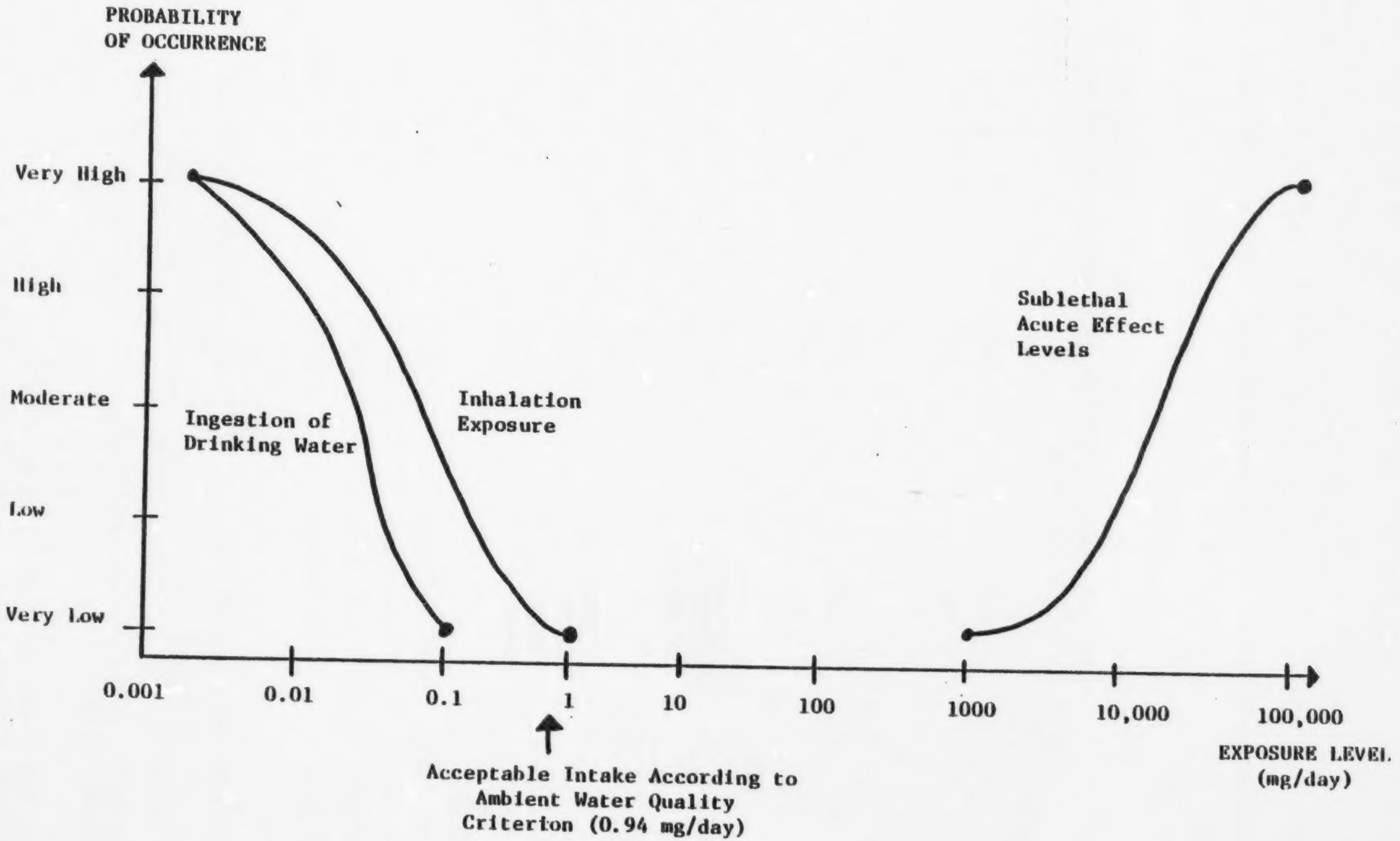

FIGURE 7-1. ACUTE EFFECT LEVELS AND DAILY HUMAN EXPOSURE FOR 1,2- AND 1,4-DICHLOROBENZENE

7.3 AQUATIC BIOTA

The lowest concentrations found to be acutely toxic to aquatic biota range from approximately 1000 ug/l to 180,000 ug/l. There was no appreciable difference in concentration levels found to be toxic to fresh and saltwater organisms. Except for increased sensitivity to 1,2-dichlorobenzene reported for two aquatic organisms, there does not seem to be an appreciable difference in toxicity among the three isomers.

Aquatic releases of the dichlorobenzenes are not very large; about 325 kkg/year (about 1.5% of the net domestic supply) 1,2-dichlorobenzene and 850 kkg/year (about 3% of the net domestic supply) 1,4-dichlorobenzene were estimated in the materials balance (Section 3.0). The discussion on the environmental fate of dichlorobenzenes released to the aquatic media (Section 4.0) suggests that any dichlorobenzene in the water column would be expected to be diluted, volatilized or adsorbed onto sediment depending on the conditions in the receiving waters. The EXAMS data suggest that these compounds will not be very persistent in the water column, and availability to the aquatic biota would be low.

Although the monitoring data for the dichlorobenzenes are limited, the concentration levels found in ambient and effluent waters are generally in the low ppb range. The unremarked STORET data include only one observation of 1,2-dichlorobenzene above 1000 μg/l in the ambient water and one observation in effluent waters. Ninety-two (92) percent of the ambient unremarked data, and 68% of the effluent unremarked data are ≤ 10 ug/l.

It appears that the average concentrations of dichlorobenzenes in the aquatic environment would not pose a severe threat to aquatic biota since very few concentrations above the threshold of effects levels have been observed, and natural fate processes for removal of dichlorobenzenes released to the environment would act to prevent long-term accumulation in aquatic systems, given the present rates of release.

However, the short-term effects of direct discharges of large quantities of dichlorobenzenes do present a risk to aquatic biota, as is apparent in reports of fish kills attributed to a chemical plant, chemical dump, and cleaning of municipal equipment. The fish kills ranged in size from 360-41,945 fish and affected from 1-4.4 miles of river. Complete data were not available, but the extent of damage is certainly dependent upon the ambient conditions of the river system. The EXAMS data in Section 4.3 indicate that most of the dichlorobenzene will be removed from the river system in a short time. This is supported by the fact that the effects of these large discharges were only observed for one day.

TABLE 7-5. CRITERIA AND STANDARDS FOR DICHLOROBENZENES

Medium	Criteria/Standard
Ambient Water	U.S. EPA - Dichlorobenzenes: <400 μg/1 for protection of human health; ingestion of water and aquatic organisms. <2.6 mg/1 for ingestion of aquatic organisms only. Soviet Union - 2 μg/1 for 1,2- and 1,4-dichlorobenzene.
Workplace (OSHA)	1,2-Dichlorobenzene: 300 mg/m^3 ceiling level. 1,4-Dichlorobenzene: 450 mg/m^3 8-hr, time-weighted average.

APPENDIX A

Table A-1. Dichlorobenzene Emission Factors

Source	Emission Factor: kg lost/kg produced (used)			
	Process	Storage	Fugitive	Total
o-Dichlorobenzene Production	0.00232	0.00047	0.00076	0.00355
p-Dichlorobenzene Production	0.00581	0.00041	0.00102	0.00724
o-Dichlorobenzene Uses:				
3,4-Dichloroaniline Manufacture	0.00105	0.00015	0.00030	0.00150
Dye Synthesis	0.00040	0.00005	0.00005	0.00050
Pesticide Intermediate	0.00040	0.00005	0.00005	0.00050
p-Dichlorobenzene:				
Pesticide Intermediate	0.00040	0.00005	0.00005	0.00050

Source EPA, 1980e.

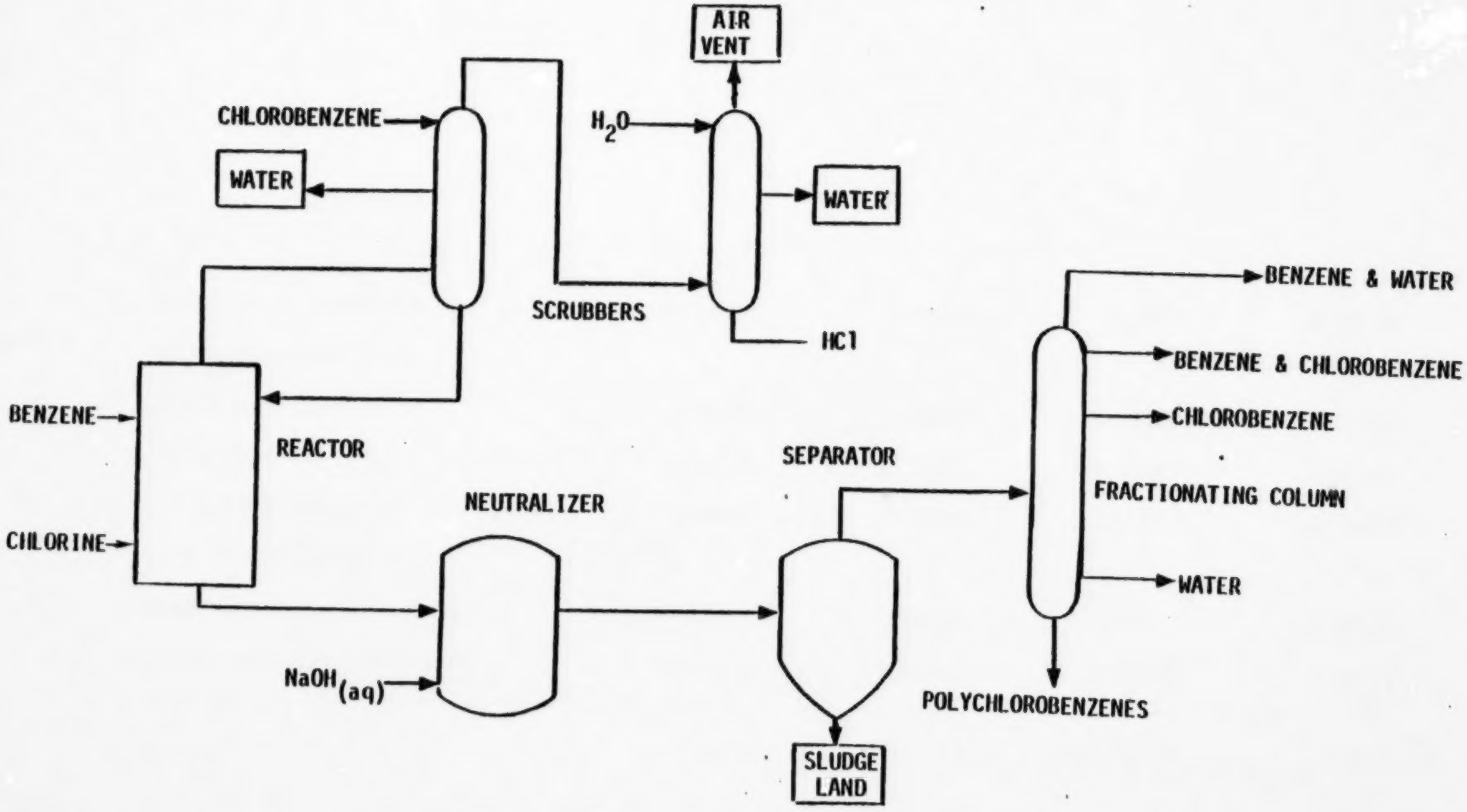
AIR VENT
CHLOROBENZENE
H_2O
WATER
WATER
SCRUBBERS
HCl
BENZENE & WATER
BENZENE & CHLOROBENZENE
CHLOROBENZENE
BENZENE
REACTOR
SEPARATOR
FRACTIONATING COLUMN
NEUTRALIZER
CHLORINE
WATER
$NaOH_{(aq)}$
POLYCHLOROBENZENES
SLUDGE LAND

Figure A-1. Batch Production of Chlorobenzenes and Environmental Release Points for Dichlorobenzenes (Lowenheim and Moran, 1975)

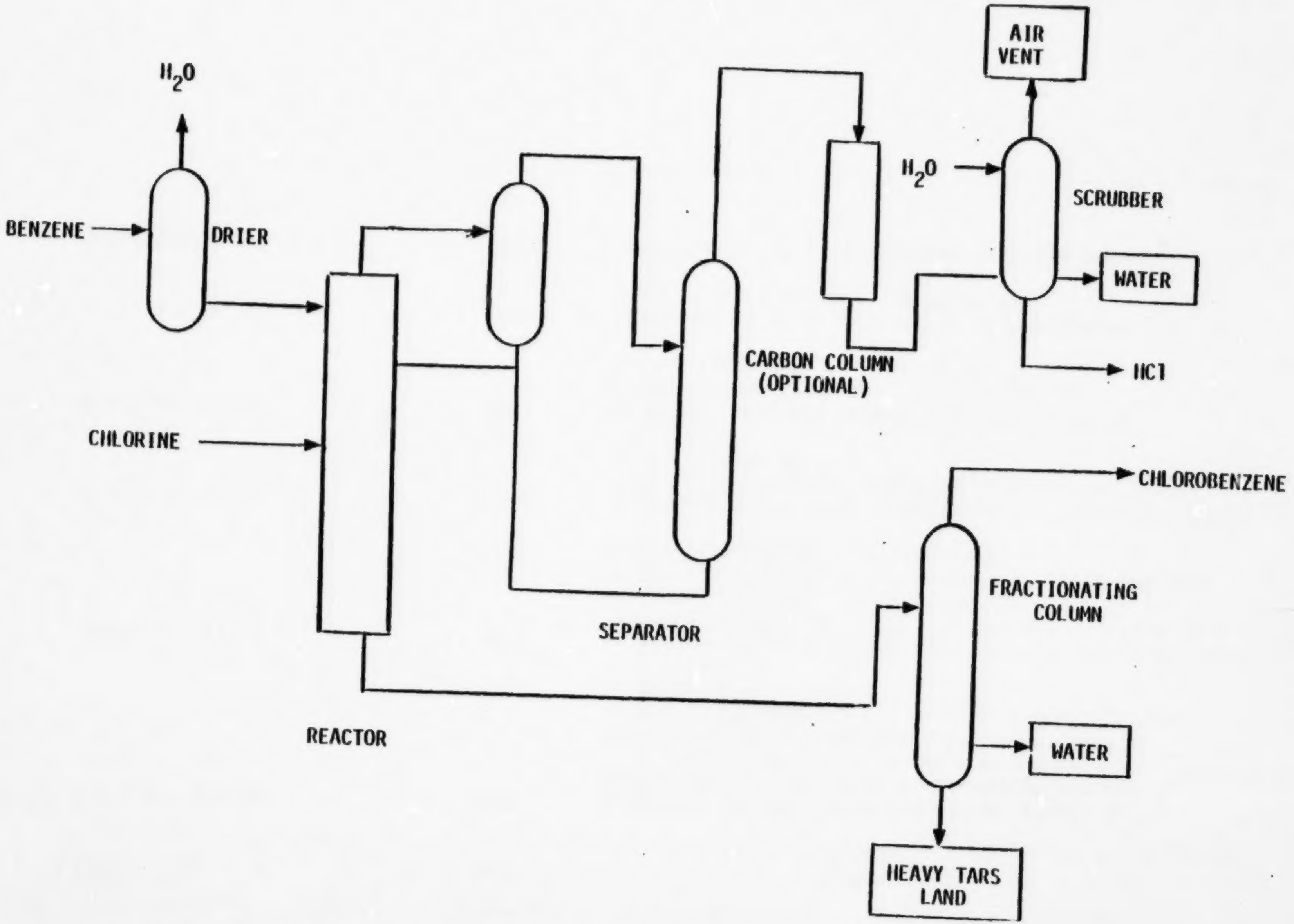
BENZENE
H_2O
DRIER
CHLORINE
REACTOR
SEPARATOR
CARBON COLUMN
(OPTIONAL)
H_2O
AIR
VENT
SCRUBBER
WATER
HCl
CHLOROBENZENE
FRACTIONATING
COLUMN
WATER
HEAVY TARS
LAND

Figure A-2. Continuous Production of Chlorobenzene and Environmental Release Points for Dichlorobenzene (Lowenheim and Moran, 1975)

Table A-2. Patents Relating to Meta-Dichlorobenzene Manufacture

Patent (Country)	Date	Purpose
2,186,454 (France)	1972	To produce DCB with high proportion of meta by thermal dechlorination of hexachlorocyclohexane. using parraffins (C_{24}+) as chlorine acceptors. Composition of chlorobenzene mixture obtained is typically 40% mono and di: 5% mono, 29% meta,+ para, 6% ortho (200° - 300°C).
2,943,114 (U.S.)	1960	To produce meta-DCB by hydrogenolysis of tri-chlorobenzenes. Yields of 33% DCB in example, distributed 39% meta, 25% para. Vapor state (300 - 600°C). Yield can be increased by chlorinating ortho and para to trichlorobenzenes and recycling.
2,920,109 (U S.)	1960	To produce meta-DCB by isomerization of para-DCB (pure or in a mixture of DCB's) by heat under pressure. Yields 90%.
2,866,828 (U.S)	1958	To produce meta-DCB from tri-chlorobenzenes by reduction with hydrogen. Yields based on tri-chlorobenzenes mixture are 17.2% (ex.)
2,819,321 (U.S.)	1958	Isomerization of o, p to m-DCB: high pressure. 120°C. 40% conversion anhydrous HCl.
2,666,085 (U.S.)	1954	Isomerization of o, p to m-DCB: water is present.

Table A-3. National Organic Monitoring Survey, March 1976 through January 1977

Isomer	Phase[a]	Number of Positive Analyses per Number of Analyses			Mean Concentration (μg/l) Positive Results Only			Median Concentration (μg/l) All Results[b]		
		I	II	III	I	II	III	I	II	III
o-DCB			0/113	4/110			1.5		<0.005	<0.005
m-DCB			0/113	2/110			0.10		<0.005	<0.005
p-DCB		2/111	20/113	29/110	2.0	0.14	0.07	<1	<0.005	<0.005

a) Monitoring dates: Phase I: March - April, 1976
Phase II: May - July, 1976
Phase III: November, 1976 - January, 1977.

b) These are minimum quantifiable limits

Source: EPA, 1977f.

Table A-4 Ambient Levels of Dichlorobenzenes in Water[a]

Levels/Isomer	Comments
1.0 ug/l, o-DCB 0.5 ug/l, m-DCB 0.5 ug/l, p-DCB	Miami, FL; ground water; CCE
d, all isomers	Miami, FL, ground water; VOA[b] Philadelphia, PA, raw water contaminated with municipal waste; VOA Cincinnati, OH; raw water contaminated with municipal waste or industrial discharge; VOA
d, m-DCB and p-DCB[b]	Lawrence, MA; raw water contaminated with industrial discharge; VOA
690 ug/l, o-DCB[c] 33 ug/l, DCB[c]	Catawba River, NC; industrial discharge; FID[c]
30-400 ug/l, o-DCB[d] 34-230 ug/l, p-DCB[d]	Summer-Fall concentrations in submarine sewage (7-mile) effluent; Hyperion Treatment Works, Los Angeles, CA. Los Angeles, CA.
4.7-2.3 ug/l, o-DCB[d] 9.3-3.1 ug/l, p-DCB[d]	Summer-Fall concentrations in submarine outfall, sewage treatment effluent, Pt. Loma, CA.
0.01 ug/l, o-DCB[d] 0.05 u/l, p-DCB[d]	Surface runoff to Los Angeles River
<0.005 ug/l, all isomers[e]	Terminal values for samples of U.S. drinking water U.S. EPA-NOMS study (see Appendix A).
1 µg/l, o-DCB[b] <3 µg/l, m-DCB[b] 1 µg/l, p-DCB[b]	Highest concentrations reported, as of 1975, U.S. drinking waters.

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a) Includes raw, discharge and drinking waters
b) EPA, 1975b; d = detected but not quantified; VOA volatile organic analysis; CCE = carbon/chloroform extract.
c) EPA, 1977e, as cited in EPA, 1977a; FID = flame ionization detector.
d) Young *et al*., 1976, as cited in EPA, 1977a.
e) EPA, 1977f.

APPENDIX B

Table B-1. Frequency of Dichlorobenzene Detection in Industrial Wastewaters

Industry	# Samples	# found		
		1,2-	1,3-	1,4-
Adhesives and Sealants	11	0	1	0
Leather Tanning	81	15	4	15
Textile Products	121	12	0	4
Printing and Publishing	109	4	1	4
Pesticides	147	2	2	2
Pharmaceuticals	95	1	0	2
Organics and Plastic	723	16	13	23
Steam Electric Power Plants	84	----------17----------		
Iron and Steel	431	1	1	3
Foundries	54	0	2	0
Nonferrous Metals	173	0	2	2
Photographic	25	1	1	1
Inorganic Chemical	107	1	0	1
Electrical	35	4	0	2
Auto and Other Laundries	56	5	0	7
Landfill	7	1	0	0
Mechanical Products	35	0	0	5

Source: EPA, 1980g

Table B-2. 3,4-Dichloroaniline Producers

Producer[a]	Location	1,2-Dichlorobenzene Releases		
		Air[b]	Water	Land
Blue Spruce Co.	Bound Brook, NJ	8		
E.I. du Pont de Nemours & Co., Inc. Chemicals, Dyes and Pigments Dept.	Deepwater, NJ	8		
Monsanto Co. Monsanto Industrial Chemicals Co.	Luling, LA	8		
Total		24		

---

a) Production capacities were not available; SRI, 1979b.

b) See Table A1 for emission factors; total broken down into process (70%), storage (10%) and fugitive (20%).

Table B-3 o-Dichlorobenzene Emission from Toluene Diisocyanate (TDI) Producers

Producer[a]	Location[a]	TDI Capacity[a] (10^3 kkg/yr)	1,2-Dichlorobenzene Releases		
			Air[b]	Water	Land
Allied Chemical Corp. Specialty Chemicals Div.	Moundsville, WVA	36	380		
BASF Wyandotte Corp. Polymers Group Urethane Div.	Geismar, LA	45	480		
Dow Chemical U.S.A.	Freeport, TX	45	480		
E.I. du Pont de Nemours & Co., Inc. Elastomer Chemicals Dept.	Deepwater Point, NJ	32	340		
Mobay Chemical Corp. Polyurethane Div.	Cedar Dayou, TX	59	630		
	New Martinsville, WV	45	480		
Olin Corp. Olin Chemicals Group	Ashtabula, OH	14	150		
	Lake Charles, LA	45	480		
Rubicon Chemicals	Geismar, LA	18	190		
Total		340	3,600		

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a) SRI, 1979b.

b) See Table A-1 for emission factor.

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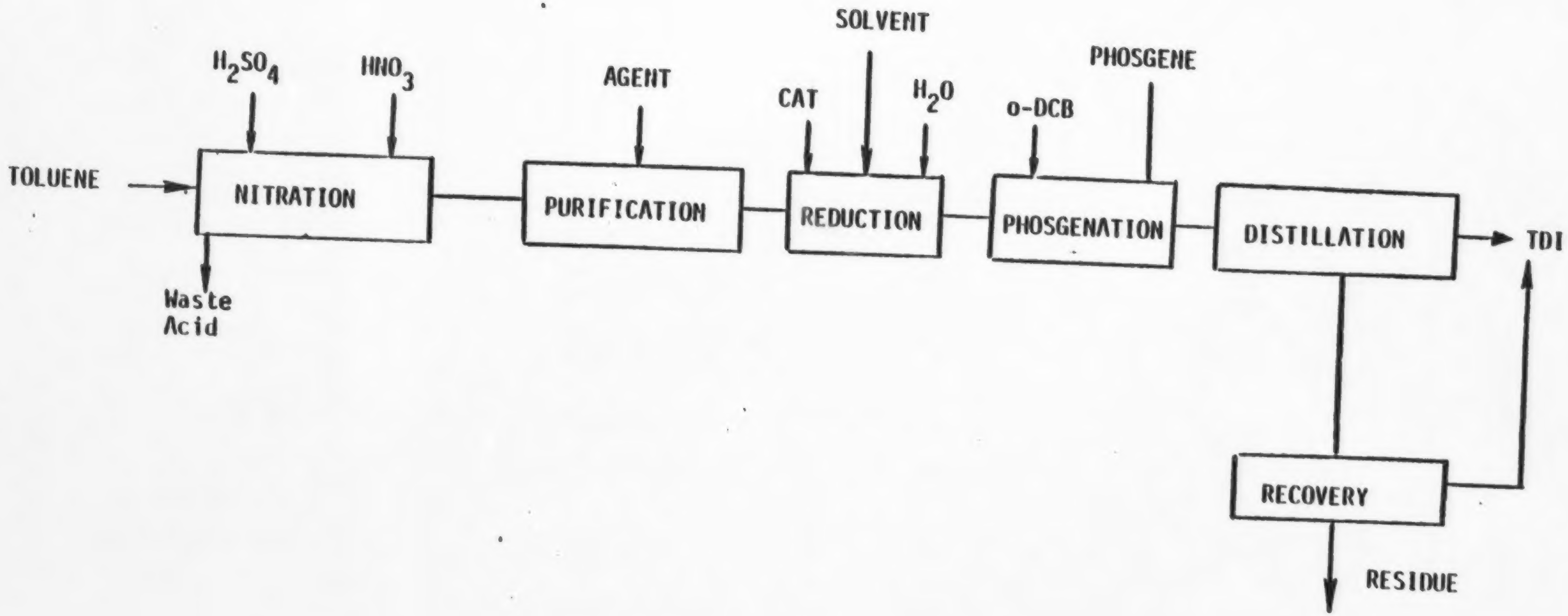
SOLVENT
H₂SO₄
HNO₃
AGENT
CAT
H₂O
PHOSGENE
o-DCB
TOLUENE
NITRATION
PURIFICATION
REDUCTION
PHOSGENATION
DISTILLATION
TDI
Waste Acid
RECOVERY
RESIDUE

Figure B-1. Block Diagram for Toluene Diisocyanate Production

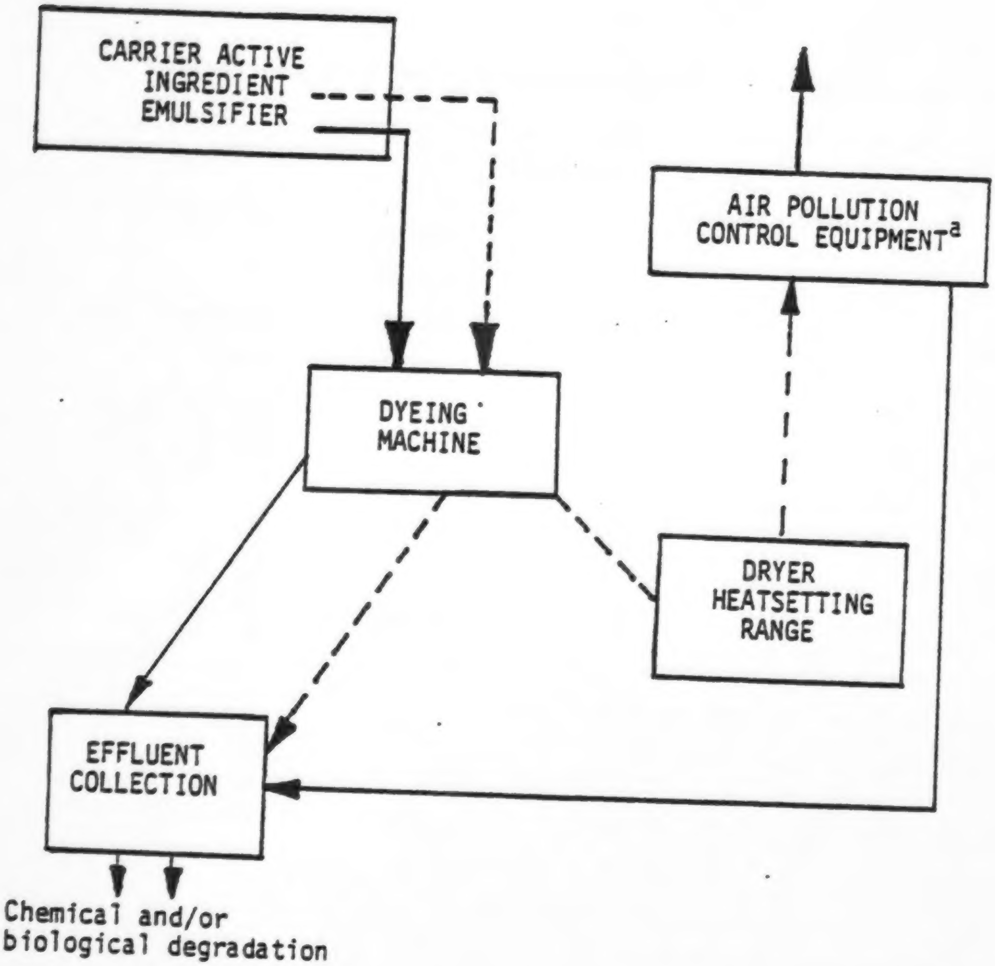
CARRIER ACTIVE
INGREDIENT
EMULSIFIER
AIR POLLUTION
CONTROL EQUIPMENT[a]
DYEING
MACHINE
DRYER
HEATSETTING
RANGE
EFFLUENT
COLLECTION
Chemical and/or
biological degradation

Figure B-2. Air and Water Pollution Control for Dye Carriers (Wannemacher and DeMaria, 1979)

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a) Probably a wet scrubber device, as the discharge is to effluent collection.

Table B-4 Dyestuffs Utilizing 1,2-Dichlorobenzene as a Reaction Solvent

Colour Index Name	Colour Index Number	Class	Manufacturers[a]
Direct Blue 106	51300	oxazine	CKC. CGY, ATL
Direct Blue 108	51320	oxazine	ATL
Direct Violet 54	51325	oxazine	no known US maker
Mordant Red 27	45180	xanthene	S (US)
Pigment Violet 23	51319	oxazine	BAY(V), CTN, ACY, SNA, GAF, S(US), HST, ALC, CGY, MM. SYN
Vat Orange 9	59700	anthraquinone	ICI(O), AAP, ACY, CGY, GAF, CKC. NCC, DUP, TR
Vat Red 10	67000	anthraquinone	GAF, ICI(O), AAP, CGY, NCC, DUP

Source: Society of Dyers and Colourists, 1971: EPA, 1977c.

a) AAP - American Aniline Products. Inc.· Paterson, NJ
ACY - American Cyanamid Co: Bound Brook, NJ
ALC - Allied Chemical Corp. (Buffalo Color and Chemical), Paterson, NJ
ATL - Atlantic Chemical Corp., Nutley, NJ
BAY(V) - Verona Division of Baychem Corp., Union, NJ
CGY - CIBA - GEIGY Corp., Ardsley, NY
CKC - Crompton and Knowles Corp., Fairhawn, NJ and Skokie. IL
CTN - Chemetron Corp., Holland, MI
DUP - E. I. du Pont de Nemours and Co., Inc., Wilmington, DE
GAF - GAF Corp., New York, NY
HST - American Hoescht Corp., Somerville, NJ
ICI(O) - ICI America Inc., Wilmington, DE
MM - Martin-Marietta Corp., Sodyeco, NC
NCC - Nyanza, Inc., Lawrence, MA
S(US) - Sandoz Colors and Chemicals. East Hanover. NJ
SNA - Sun Chemical Corp., Staten Island, NY
SYN - Synalloy Corp., Spartanburg, SC
TR - Toms River Chemical Corp., Toms River, NJ

Table B-5 Ambient Levels of Dichlorobenzenes in Air

Levels/Isomer	Comments
2 1 to 4.2 g/m^3, p-DCB[a]	Tokyo Metropolitan Area
trace, o-DCB[b]	Rural California
25-35[c], 70[c] ppm p-DCB	Workplaces associated with manufacture of p-DCB
<1.0 ppm[d]	Monochlorobenzene manufacturing plant
<8 ng/m^2-day, o-DCB[e]	Catalina Island aerial fallout, high-volume sample.
27 ng/m^2-day, o-DCB[e]	San Clemente Island, aerial fallout, high-volume sample
<53 ng/m^2-day, o-DCB[2]	Santa Barbara, aerial fallout, high-volume sample
1700 μg/m^3, p-DCB[a]	Wardrobe (mothballs)
315 μg/m^3, p-DCB[a]	Closet (mothballs)
105 μg/m^3, p-DCB[a]	Bedroom (mothballs)

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a) Morita and Ohi, 1975.

b) EPA, 1978b.

c) Pagnotto and Walkley 1965.

d) SRI, 1979b; no DCB isomer specified.

e) Young et al., 1976, as cited in EPA, 1977a.